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XXXIII. *The Photoelectric Effect in Potassium Vapour as a Function of the Frequency of the Light.* *By* ERNEST ORLANDO LAWRENCE*, *M.A., Sloane Fellow in Physics, Yale University*†.

Introduction.

BECAUSE of our ignorance of the precise nature of the ejection of electrons by light from solid surfaces, that is to say, because of the complexities involved in the photoelectric mechanism for solids which the Bohr theory has not yet encompassed, experimental facts of this sort do not bear vitally on the Bohr conceptions. On the other hand, experimental data on the photoelectric effect in vapours have a direct significance in the Bohr theory, inasmuch as in this instance the atoms are isolated and free to act the *rôle* to which the theory applies. Information of the latter sort is meagre. Steubing ‡ has described an experiment which seemed to show ionization in mercury vapour by light transmitted through fused quartz. Anderson § and Gilbreath ‖ have obtained ionization in potassium vapour which they attribute to a photoelectric effect in the vapour, but which probably resulted from a photoelectric effect from the electrodes. Kunz and Williams ¶ have observed

* A dissertation presented for the degree of Doctor of Philosophy at Yale University.
† Communicated by Professor W. F. G. Swann.
‡ *Phys. Zeit.* x. p. 787 (1909).
§ Phys. Rev. i. p. 233 (1913).
‖ Phys. Rev. x. p. 166 (1917).
¶ Phys. Rev. xv. p. 550 (1920); xxii. p. 456 (1923).

a photoelectric effect in cæsium vapour having a threshold coincident with the limiting frequency of the principal series of the vapour, and Williamson * has indicated that the threshold for potassium vapour lies between 2800 Å. and 3100 Å., and has also shown that the efficiency of the light in producing the effect increases rapidly with the frequency. The present paper is an account of an experimental investigation of a more quantitative nature of the photoelectric effect in potassium vapour.

Experimental Arrangements.

The investigation of the photoelectric effect in vapours involves fundamental experimental difficulties, some of which are augmented when potassium vapour is used. It is well known that potassium is exceedingly active photoelectrically and thermionically, and the difficulties in differentiating a true photoelectric effect in the vapour from thermionic currents and photoelectric currents from the electrodes and other portions of the chamber are obvious. Various experimental methods were tried, culminating in the adoption of a method similar to that which Williamson used in his investigation. It became clear that the electrodes involved in measuring the ionization had to be kept at a temperature low relative to the temperature of the vapour requisite to produce sufficient vapour density. To meet this condition a jet of potassium was caused to traverse a chamber and condense on a liquid-air-cooled surface. The ions produced by light passing through the jet of vapour were collected by an arrangement of electrodes in a cool portion of the chamber. A collimating and diaphragming system caused the light to traverse the jet without impinging on metal parts of the chamber, thereby reducing to a minimum spurious photoelectric effects. In this way thermionic effects were reduced to a negligible order of magnitude, and restricted photoelectric effects from the electrodes and other portions of the chamber practically to effects arising from light scattered by the vapour.

The experiment was primarily a determination of the magnitude of the photoelectric ionization in the vapour per unit intensity of light as a function of the frequency. Hence a source of monochromatic light sufficiently intense to produce measurable photoelectric effects, and a means of measuring the light of intensity simultaneously with the observation of the effect in the vapour, were essentials.

* Phys. Rev. xxi. p. 107 (1923).

Preliminary experiments showed that quartz-mercury lamps were totally inadequate sources of illumination, and that light from a Pfund iron arc resolved into bands of from forty to eighty ångströms produced measurable ionization in the potassium vapour. It perhaps is of interest to note in this connexion that the photoelectric effects in the vapour produced by these relatively small bands of wave-lengths from the iron arc were as large as the effects obtained from the whole spectrum of a quartz mercury lamp. The intensity of the light was measured by a potassium photoelectric cell which in turn was calibrated by a thermopile and galvanometer.

Figs. 1 and 1*b* show diagrammatically the arrangement of the apparatus. Distilled potassium K in the reservoir R

Fig. 1.

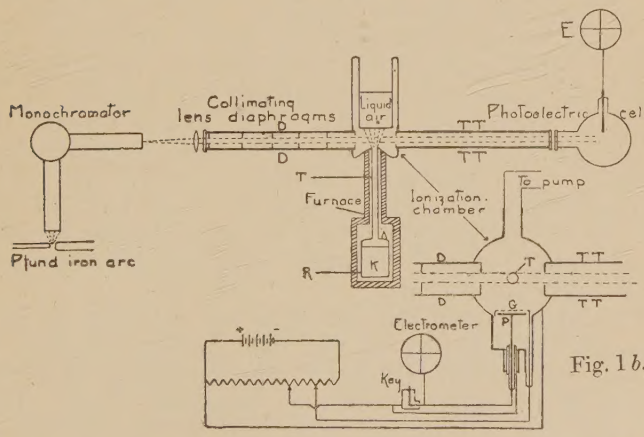


Fig. 1*b*.

was heated by a furnace, causing a jet of vapour to issue up through a tube T (20 cm. in length) into the ionization chamber and on to a liquid-air-cooled surface, as the dotted lines indicate. Of course the jet was in no sense of the word unidirectional, and a good portion of the vapour entering the chamber condensed on portions of the chamber other than the liquid-air flask. Dotted lines also indicate the course of the light which, originating in the Pfund arc, passed into a monochromator. The band of wave-lengths from the monochromator after collimation by a quartz lens passed through a quartz window into a tube D (50 cm. long) containing a series of diaphragms. From the diaphragms the light passed into the ionization chamber, traversing the stream of vapour and out through a diaphragm into a

second tube TT, and finally out through a quartz window into an adjacent photoelectric cell. The last diaphragm of the series in tube D was larger than the others, so that sensibly none of the light in the beam impinged on it. This last diaphragm cut off from the ionization chamber diffusely scattered light in the tube D, which was due to reflexions of the beam from the edges of the adjacent diaphragms. The single diaphragm in tube TT also was larger than the cross-section of the light beam, so that no portion of the bean suffered reflexion back into the chamber before entering the tube. The diagram does not properly indicate the orientation of the quartz window at the end of TT, as it was mounted so that the normals of its surfaces were at an angle with the direction of the beam of light passing through. This caused reflected light to strike the walls of the tube and to experience many reflexions before re-entering the ionization chamber. Both the interior of the tubes and the diaphragms of D and T were black. This optical system accomplished the purpose of preventing light from the monochromator striking any portion of the chamber appreciably (visible light passed through the chamber in this manner produced no discernible illumination therein). As has been mentioned before, this rather elaborate system of collimation of the beam was necessary, as without it stray light falling on the electrodes produced large spurious effects. This fact revealed itself early in the preliminary experiments.

The photoelectric cell placed at the exit end of TT to measure the intensity of the light passing through the vapour was of the Hughes * type, consisting of a flask coated on the interior with pure potassium metal. Light entering the cell through a quartz window experienced many reflexions on the potassium surface, thereby producing relatively large photoelectric currents in the cell. The sensitivity of the cell could have been further increased in the well-known manner by the introduction of suitable gases, but it was desired to have the potassium surfaces as free from contamination as possible, in order that existing data on the photoelectric selectivity of potassium could be made use of in a qualitative way. The diagram indicates an electrometer E attached to the cell. The electrometer measured the currents in some instances by the simple rate of deflexion method, and at other times the electrometer measured the fall in potential which the photo currents

* Hughes, Phil. Mag. xxv. p. 679 (1913).

produced in passing through india ink resistance of the order of magnitude of 10^{10} ohms. The india ink resistance method ultimately was used entirely, as it was found in every respect more desirable.

The furnace surrounding the reservoir and jet tube was of brass tubing wound with resistance coils embedded in alundum cement, and was insulated thermally by asbestos. It possessed sufficient "heat inertia" to ensure that temperature changes were slow.

Fig. 1 *b* is a horizontal section of the ionization chamber depicting the electrode arrangement. The circle in the centre D represents the jet, and the dotted lines indicate the course of the light in its passage through the chamber across the vapour. The electrodes G, P are in a cool portion of the chamber at the side of the vapour jet. Because of the abundance of stray electrons of thermionic origin always present, the positive ions formed in the jet by the light were measured. An accelerating potential (relative to the positive ions) between the walls of the chamber and a grid G drew the positive ions to the grid, where a good share passed through and after traversing a smaller retarding field impinged on a plate P. An attached electrometer system deflected this positive ion current on to the plate. As was the case for the photoelectric cell currents, in this instance also both the rate of deflexion method and the high resistance method were used, culminating in the adoption in the final experiments of the latter. For simplicity the diagram indicates the arrangement for measuring the positive ions by the rate of deflexion of the electrometer. The modification involved in using the resistance method is perfectly obvious. For the rate of deflexion method an electrometer sensitivity was used of 800 mm. per volt, while for the resistance method the Dolezalek electrometer had a sensitivity of 6000 mm. per volt at a scale distance of 1·6 m. and was critically damped. The resistances used were of the order of 5×10^{12} ohms, and were made of fine ruled lines of india ink on paper hermetically sealed in glass tubes.

Constructional details of the apparatus hardly merit further description. Suffice to say that the ionization chamber and the tubes D and TT with diaphragms were of brass, and the jet and reservoir and the liquid-air flask were of pyrex glass and were attached to the brass ionization chamber by wax joints. Because of the high temperature of the jet an air blast played over the wax joint, keeping it properly cooled.

Mercury diffusion pumps in conjunction with a liquid-air trap and McLeod gauge comprised the vacuum system.

Experimental Procedure.

The ionization chamber (and appending parts) was exhausted by the pump system to pressures which registered on a McLeod gauge less than 10^{-5} mm. of mercury. This vacuum was maintained during the course of a day, during which time potassium metal was distilled into the boiler. From the time of distillation of the metal to the completion of an experimental run the pumps were kept on the apparatus, thereby continually removing gases evolved from the metal and other portions of the chamber. After the completion of the distillation of the potassium into the apparatus immediately the iron arc and monochromator were adjusted so that light of maximum intensity passed through the chamber. Clearly this was obtained by an adjustment for a maximum current from the photocell. The furnaces were then turned on and brought to a fairly constant temperature in the neighbourhood of 300° C., and with suitable potentials on the electrodes the apparatus was ready for the observation of the photoelectric effects.

Preliminary experiments had shown that light of wave-length greater than 3000 ångströms apparently produced no appreciable photoelectric effects in the vapour, so that wave-lengths only of this order or shorter were used in the final experiments. It was found that a fairly intense band of wave-lengths emerged from the monochromator set at 2560 angströms (with slit-widths of 1 mm.), which produced a very readily measurable effect in the ionization chamber. The monochromator was set at this adjustment at the beginning of a run, and when conditions became steady, that is to say when both photo currents were observed to be quite constant, their magnitudes were taken down, and immediately the monochromator was adjusted to a new wave-length setting and the new values for the photo currents were noted. Next an observation with the former setting was made as a check on any change in conditions between observations. Clearly this procedure of taking observations in groups of three wherein the first and third were for the same wave-length permitted a close check on the variation of such things as the vapour density in the jet. This method of observation was extended over the whole range of useful wave-lengths, that is to say from 2200 ångströms on up. Inasmuch as the vapour rapidly distilled

out of the boiler, it was necessary to work as quickly as possible. Observations were taken at the rate of about one per minute, a greater speed being prohibited by the natural period and damping of the deflexions of the electrometer needles. However, inasmuch as a run lasted over two hours, it was possible to get a fair number of readings over the whole range of investigation. Perhaps it should be mentioned in this connexion that with advancing time the level of the molten potassium in the reservoir lowered, and in order to maintain the same vapour density in the jet the temperature of the furnaces was gradually raised to compensate the effect of the change in position. The approach of the complete disappearance of the potassium from the reservoir evidenced itself very markedly by a lowering of the vapour-pressure in the jet and consequent ultimate disappearance of the photoelectric currents in the ionization chamber.

As has been mentioned above, the photoelectric currents were measured either by the rate of deflexion of the electrometer needles, that is by the deflexion during a definite period of time, or by the fall in potential produced by the currents flowing through high resistances of india ink. The latter case involves simply noting the deflexion of the electrometer when things are in equilibrium, while the rate of deflexion method is liable to error unless certain considerations are recognized. If the observed deflexions are to be proportional to the currents, Professor Swann * has pointed out that the deflexions must be taken over periods of time which are multiples of the natural period of oscillation of the electrometer needle. A subsidiary requirement also is that the period of observation must not extend from the time of opening the electrometer key, but from a short time later—of the order of one or two seconds. With this in mind, the two methods gave consistent values for the observed currents.

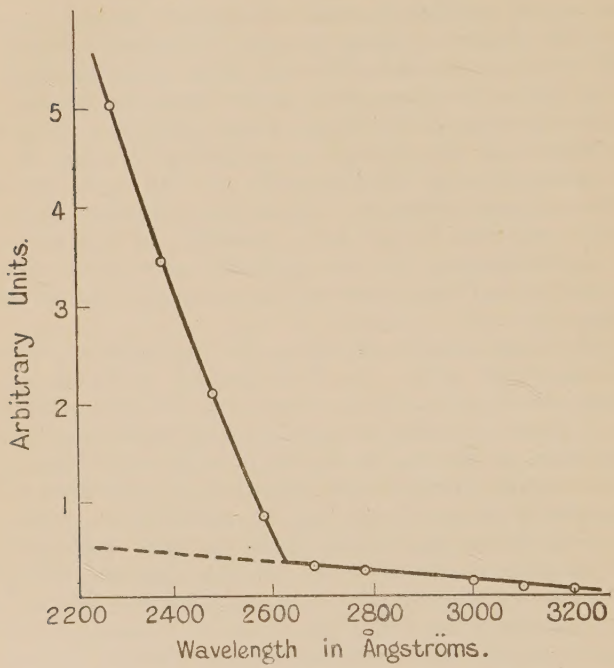
Results.

This experimental investigation was begun at the University of Chicago during the last academic year, and has been continued during the present year at Yale University. In view of the differences in the experimental apparatus at both places, it is desirable to present the results separately. As will be indicated below, the results of last year's work seemingly are at variance with what would be expected from

* Swann, Phil. Mag. xxiv. p. 445 (1912).

the Bohr standpoint, and the results of the present year form a rather significant check on the preceding year's work.

Fig. 2.—"Chicago Data."



Ordinates are ratios (arbitrary constant) :—

$$\frac{\text{Photoelectric effect in potassium vapour.}}{\text{Photoelectric effect in potassium photocell.}}$$

Abscissæ are :—

Mean wave-length of band of wave-lengths producing photoelectric effects simultaneously in vapour and in photocell.

Both photoelectric currents measured by rate of deflexion method with electrodes at following potentials :—

Walls of ionization chamber	0·0 volts.
Grid	−12·0 ,,
Plate	−10·8 ,,

The curve of fig. 2 embodies the results obtained last year at Chicago. This typical curve is for a single experimental run—that is to say, it represents the data obtained during the time that a single reservoir full of potassium distilled into the ionization chamber. The points of the curve are the averages of the observations during the run corrected

for changes in the density of the vapour-stream, as indicated in a paragraph of the experimental procedure. The ordinates are the ratios (times an arbitrary constant) of the photoelectric currents from the vapour to the photo currents from the photocell, produced by bands of wave-lengths emerging from the monochromator when adjusted at a wave-length setting given by the abscissæ. It is clear that if the photocell were equally sensitive to all wave-lengths, and the light emerging from the monochromator were monochromatic, the curve would represent the variation of the photoelectric effect in the vapour per unit light intensity with the frequency. Neither of these conditions subsisted in the experiment, so that the curve representing the variation per unit intensity with the frequency has a somewhat different form.

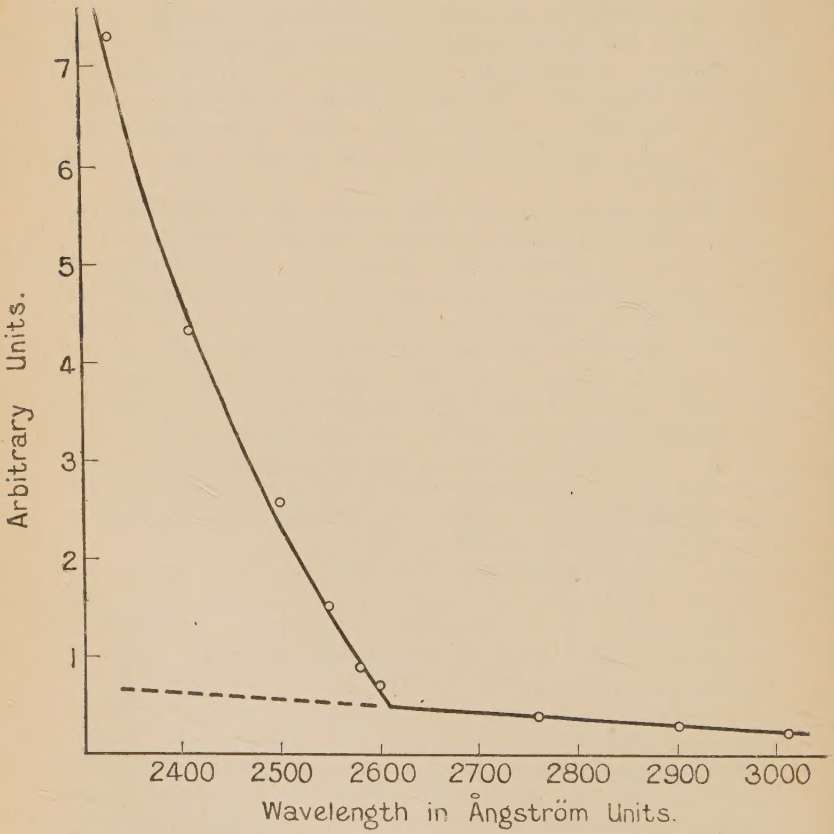
A Hilger monochromatic illuminator was used at Chicago, and the data of the above curve were obtained with slit-widths of 1·2 mm. A spectroscopic examination of the quality of the light emerging from the monochromator revealed that roughly 90 per cent. of the light was contained in bands of from fifty to a hundred ångströms (depending on the wave-length setting), which were symmetrical with respect to the wave-length for which the monochromator was adjusted. The remaining portion of the light was distributed throughout the spectral range, and of especial significance was the fact that there was always transmitted some light of much shorter wave-lengths. With this information it is possible to get at the significance of the curves.

The curve is represented quite closely by two intersecting straight lines, and is linear over intervals about the experimentally given points through which the curve is contructed. This point of intersection strikingly suggests itself as the photoelectric threshold for the vapour—that is, the abscissa of this point is the longest wave-length able to produce a photoelectric effect in the vapour. The photoelectric effects observed for wave-lengths greater than this threshold value represented by the portion of the curve to the right of the intersection are attributed to stray light of shorter wave-lengths transmitted by the monochromator, and to a photoelectric effect from the electrodes due to a small amount of scattered light.

Now let us consider the experimental points making up the portion of the curve to the left of the threshold. The photoelectric effects here arise from both stray effective wave-lengths and the bands of wave-lengths symmetrically placed about the values given by the abscissæ. Because of

the linearity of the curve over these bands, it is clear that the assigned abscissæ are approximately the effective mean values for the wave-lengths of the bands, and allowing for the stray light, this portion of the curve represents the variation of the ratio of the photoelectric effect in the vapour to the effect in the photocell with the wave-length.

Fig. 3.—"Yale Data."



Ordinates and abscissæ same as Fig. 2.

Photoelectric currents measured by high-resistance method with electrodes at the following potentials.

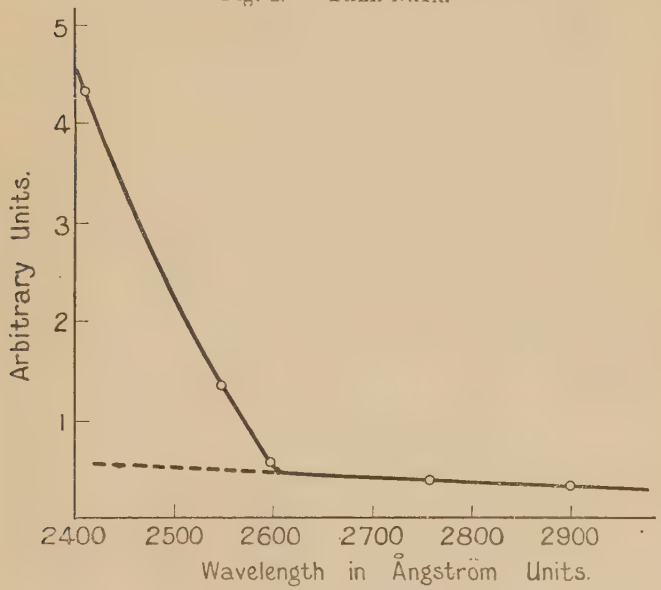
Walls of ionization chamber	0·0 volts.
Grid	−22·0 ,,
Plate	−19·8 ,,

The amount of spurious effect in this region has not been determined, but probably is not far from that obtained by

extrapolating from the portion to the right of the threshold, as indicated by the dotted lines.

Significant evidence of the trustworthiness of these results is given by the more recent experiments at Yale. The curves of figs. 3 and 4 are representative of the later results, and are seen to be of the same form as previously obtained at Chicago (fig. 2). There were two changes in the Yale apparatus of importance—namely, the monochromator and the photoelectric cell. A Gaertner instrument was used with

Fig. 4.—"Yale Data."



Ordinates and abscissæ same as for fig. 3.

Currents measured by high-resistance method with electrodes at following potentials:—

Walls of ionization chamber	0·0 volts.
Grid	−11·0 „
Plate	− 9·9 „

slit-widths of 1 mm. (giving wave-length bands of forty to eighty ångströms) and a new photocell was built similar to the one used at Chicago. In view of these changes, it is interesting to note the agreement in the threshold values obtained, an agreement perhaps more complete than should be expected. Of interest also is the similarity of the curves to the right of the threshold, which suggests that either the two monochromators are quite equally defective in their

function of producing monochromatic light, or that in all instances the amount of scattered light was about the same. This latter possibility suggests that the vapour was responsible for the scattering. The form of the results embodied in the above curves is a function of the selectivity of the photoelectric cell. This accounts for the more pronounced curvature of the Yale curves (figs. 3 and 4). Finally, the data indicate that the observed photoelectric effects in the vapour are practically independent of both the potentials on the electrodes in the ionization chamber and the condition of the vacuum. In all cases the photoelectric effects observed have been of the form exhibited above, although a range of potentials from eight to twenty-two volts has been used, and the vacuum, as indicated on a McLeod gauge, has ranged from 10^{-3} mm. to 10^{-5} mm.

Because of the difficulties in measuring light intensities in the ultra-violet, the calibration of the photocell lacked precision and was extended only to 2580 ångströms. It was found that the selectivity of the cell was qualitatively similar to that of new potassium metal surfaces as found by Souder *. On the basis of this calibration, the probable variation of the photoelectric effect in the vapour per unit intensity of light as a function of the wave-length is given by the curve of fig. 5. Although a slight curvature is exhibited—suggesting a maximum—it is entirely possible that more reliable intensity measurements will show that this is a linear relation. It is hoped that this point will be settled in the near future. For the present, it can be asserted that only light of wave-length shorter than 2610 Ångström units is able to produce a photoelectric effect in a stream of potassium vapour, and that the magnitude of the effect per unit light intensity is greater for shorter wave-lengths.

Williamson † has interpreted his results as indicating the photoelectric threshold at the Bohr theoretical value, namely 2856 angströms. However, it is interesting to note that his published data are well in accord with the value herein given. It is interesting further to observe that the present results confirm his conclusion that light of shorter wave-lengths is more efficient in producing the photoelectric effect in the vapour jet, and that the general effects observed were independent of the electrode potentials,

* Phys. Rev. viii. p. 310 (1916).
† Phys. Rev. xxi. p. 107 (1923).

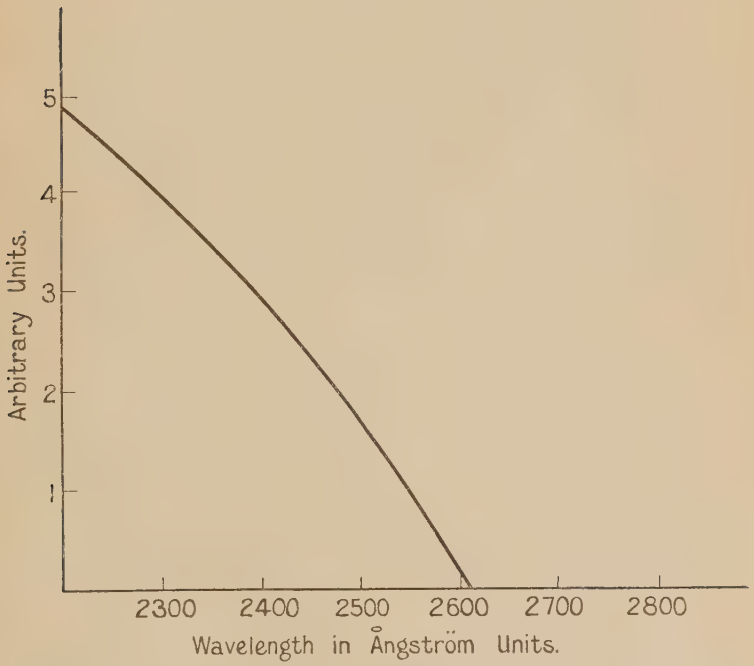
including potentials below the ionization potential of the vapour.

Discussion.

Researches on the absorption of light in alkali vapours reveal that wave-lengths of the principal series are absorbed as well as wave-lengths shorter than the series limit. The Bohr theory attributes the former phenomenon to the

Fig. 5.

Photoelectric effects in stream of potassium vapour per unit intensity of light.



Ordinates are photoelectric currents produced in vapour produced by light of wave-length given by abscissæ.

Photoelectric threshold at 2610 ångströms.

energy given up by the light in removing electrons from the 1*s* to the various *p* orbits, and the latter to a photoelectric effect. Light-quanta of greater frequency than the series limit have more than enough energy to eject an electron from the atom, and the surplus is used in giving the electron a velocity after ejection.

Corresponding phenomena occur in the X-ray region. There an absorption is observed which decreases approximately as the cube of the wave-length from the K, L, and M limits. In this instance also the absorbed energy goes into the jumps of the electrons from various orbits and their velocity upon complete removal from the atom. The velocities of these X-ray photoelectrons have been measured and found to agree with this view, and in general all the experimental evidence supports this photoelectric origin of the absorption.

Continuous optical absorption of wave-lengths shorter than the series limit has been obtained by Wood * in sodium and by Holtsmark † in sodium and potassium, and more recently Harrison ‡ has published excellent photometric measurements of the variation of the absorption with the wave-length. Harrison's results indicate that the absorption decreases with the wave-length from the series limit in a manner similar to the decrease beyond the absorption limits in the X-ray region. By analogy with the X-ray photoelectric data this similarity suggests that this continuous absorption is due to a photoelectric effect in the vapour, in agreement with the Bohr theory. However, as has been pointed out, direct photoelectric evidence is meagre, and the present research was initiated with the hope of obtaining more definite data of this sort.

Williamson has discussed in detail the experimental evidence from which is concluded that the effects observed are photoelectric effects in the vapour. In the present instance it is sufficient to say that his evidence and conclusions have been confirmed. Now, clearly, the results obtained are completely in disaccord with expectations. Neither does the photoelectric threshold coincide with the limiting wave-length of the principal series, nor is the light of wave-length just less than the threshold the most effective in producing the photoelectric effect. If these results are truely representative of the photoelectric effect from potassium atoms in the vapour, we have here an apparent serious difficulty for the Bohr theory.

The most plausible explanation of the difficulty is that the vapour consists of aggregates of potassium atoms, most probably in a sort of diatomic molecular form. Then, if an energy of ·4 volt is assigned to that involved in dissociation,

* Astrophys. Journ. xxix. 97 (1909).
† *Phys. Zeit.* xx. p. 88 (1919).
‡ Phys. Rev. xxiv. p. 466 (1924).

we have as the total energy required to ionize a molecule

$$\underset{\text{(Dissociation)}}{\text{·4 volt}} + \underset{\text{(Ionization)}}{\text{4·3 volts}} = \text{4·7 volts},$$

corresponding to the energy of a quantum of wave-length herein given as the threshold, viz. 2610 ångströms. That the vapour is in a molecular state receives support from other sources. Professor Wood * has observed channelled absorption bands in sodium vapour, and more recently H. D. Smith † has shown band absorption in potassium and other alkali vapours which strikingly suggests that a portion of the vapour is molecular. Clearly, if the number of such molecules is small relative to the number of atoms, the fact that the atomic photoelectric effect is not observed may be stated in another form, namely that the probability of a light-quantum ionizing a molecule is greater than that of its ionizing an atom.

Experiments are in progress designed to measure the initial velocities of the photoelectrons, and a method of positive-ray analysis is being developed to ascertain the nature of the photoelectric ions. Further theoretical speculation will be held in abeyance pending the outcome of this work.

Summary.

The photoelectric effect in a stream of potassium vapour has been observed, and it has been found that light of wave-length greater than 2610 ångströms produces no effect, and that the efficiency of the light in producing ionization increases as shorter wave-lengths are used. Because of the inconsistency with the Bohr theoretical interpretation of spectroscopic data on atomic potassium, the photoelectric effects observed are regarded as most probably due to a molecular state of the vapour.

The writer is very grateful to Professor W. F. G. Swann, who suggested the research, for his continued interest and many invaluable suggestions and criticisms throughout the course of the work, both at Chicago where the investigation was commenced and at Yale where it was completed.

Sloane Laboratory,
Yale University,
February 2, 1925.

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* Wood, 'Physical Optics,' 2nd edition.
† Smith, Proc. Roy. Soc. cvi. p. 400 (1924).

XXXIV. *Note on Mr. Garner's Paper on the Critical Increment of Chemical Reactions.* *By* C. N. Hinshelwood, *Trinity College, Oxford* *.

THE occurrence of a bimolecular reaction in a gaseous system seems to depend upon collisions between molecules with high kinetic energy. Using an approximate form of the Maxwell distribution law this assumption leads to the following expression for the velocity constant k of the reaction

$$k = 2 \times \text{total number of collisions} \times e^{-Q/RT} \times P,$$

the factor $e^{-Q/T}$ giving the fraction of the total number of collisions in which the energy is sufficiently great The factor 2 is introduced because each fruitful collision involves the change of two molecules. P is a factor depending on the shape of the molecules (and possibly on internal "phase" factors) which expresses the probability that a collision between activated molecules results in the formation of the reaction products rather than in the separation of the two molecules in a chemically unchanged state.

Experimental evidence shows that P is of the order of magnitude unity—a result of considerable interest. Unless Q could be determined with a quite unattainable degree of precision, the nature of the above equation makes it impossible to ascertain the exact value of P. Nevertheless the knowledge that it is of the order of unity permits an absolute calculation of the logarithm of a velocity constant from the value of the heat of activation Q, in a manner well confirmed by experiment.

Q is obtained from the temperature-coefficient of k. The collision number is proportional to $\sqrt{T}$, whence

$$k = \text{constant } \sqrt{T}\, e^{-Q/RT};$$

$$\text{thus} \qquad d \log k/dT = \frac{1}{2T} + Q/RT^2.$$

In a recent communication to the Philosophical Magazine (1925, vol. xlix. p. 463) Mr. Garner points out that P cannot be exactly equal to unity. But it may be replied that in "irreversible" reactions there is no reason why P should not approach unity almost indefinitely. He also suggests that since P itself is an unknown function of temperature, the method of determining Q from the effect of temperature on the reaction velocity is unsound.

* Communicated by the Author.

Unless I have misunderstood Mr. Garner's argument this criticism is not valid. Perhaps, at all events, it may be permissible to state the alternative view.

Temperature has no meaning applied to individual molecules. It defines the statistical distribution of energy among large numbers of molecules. Activated molecules are molecules with specified energies. Temperature determines how many of these exist and how many collisions take place between them. Whether a collision between two individual molecules with specified energies is "elastic" or "inelastic" in the chemical sense cannot depend upon the distribution of energy among other molecules which are not participating in the impact. Thus P would seem to be independent of temperature. "Activated" molecules have always the same "temperature" whatever the real statistical temperature of the gas may be, because they are *ex hypothesi* molecules of specified energy.

The use of the distribution law in the form $e^{-Q/RT}$ is of course not quite unobjectionable theoretically, but is justified by experiment within the limits of accuracy obtainable in the determination of Q.

Trinity College, Oxford.

XXXV. *Refraction and Electron Constraint in Ions and Molecules.* *By* Charles P. Smyth, *Ph.D., Department of Chemistry, Princeton University* *.

IN the problems of molecular structure and chemical activity the outer electrons of the atomic shells are of prime importance and the constraints under which these electrons act may be decisive factors in determining the molecular behaviour. An approximately quantitative measurement of these constraints may be obtained from a consideration of the force necessary to displace the electrons from their positions of equilibrium or to alter or distort their orbits in the molecule. In the present discussion such an alteration or distortion will be treated as equivalent to a displacement of the effective position or position of equilibrium of the electron in the molecule. The force necessary to displace an electron may be calculated on the assumption that, when a small displacement occurs, the force tending to

* Communicated by the Author.

restore the electron to its original position is proportional to the amount of the displacement, that is

$$\text{restoring force} = f \times \text{displacement},$$

in which f is a proportionality constant. When the displacement is unity, the restoring force is f, or f is the force which would be required to displace an electron one centimetre from its normal position in a molecule if the restoring force were always proportional to the displacement. Obviously, the relation cannot hold for a displacement of this magnitude, but, for very small displacements, such as those which cause refraction, it may be regarded as holding approximately. The constant f thus provides a measure of the resistance to the displacement of the electron.

In a previous paper* the writer has calculated f from relations which, for the purpose of the present paper, may best be expressed by the equation

$$\frac{m_\infty^2 - 1}{m_\infty^2 + 2} = \frac{4\pi \mathrm{N} e^2}{3f},$$

in which m_∞ is the refractive index for light of infinite wave-length, N is the number of electrons in unit volume suffering displacement, and e is the electronic charge. This, by simple substitutions, may be converted to

$$f = \frac{4\pi \mathrm{N}_0 n e^2}{3} \left(\frac{d}{w} \frac{m_\infty^2 + 2}{m_\infty^2 - 1} \right),$$

in which N_0 is Avogadro's number, $6{\cdot}061 \times 10^{23}$, n is the number of displaceable electrons per molecule, d is the density, and w is the molecular weight; or

$$f = \frac{4\pi \mathrm{N}_0 n e^2}{3\mathrm{M}_\infty},$$

where M_∞ is the molecular refraction for light of infinite wave-length. In the paper referred to f was calculated for a number of gases and, as great accuracy was neither required nor possible, refractive indices for light of visible wave-length were commonly used.

In a paper immediately subsequent to this, Born and Heisenberg† have used a somewhat similar expression to calculate the deformability, α, of an ion, α being defined by

* C. P. Smyth, Phil. Mag. xlvii. p. 530 (1924).

† M. Born and W. Heisenberg, *Z. Physik*, xxiii. p. 388 (1924).

the relation $p = \alpha E$, in which p is the moment induced by a homogeneous electric field, E. The relation of α to f is given by the expression :

$$\alpha = \frac{ne^2}{f}.$$

By a combination of these calculations from refractive indices with deductions from values for the terms of spectral series, Born and Heisenberg obtained the deformability of the ions of a large number of elements. It is evident that α is proportional and f inversely proportional to the molecular or ionic refraction, and Fajans and Joos * have used the refraction as a direct measure of the deformability of the electron shells. These investigators have calculated the molecular refractions for the D-line, obtaining results in fair agreement with those for the D-line obtained by Wasastjerna for the rare gas atoms and a number of ions in an earlier investigation † and with those calculated from the values of α given by Born and Heisenberg. The refractions calculated for infinite wave-length should provide a sounder theoretical basis for the treatment of the electron constraints, but as the difference in wave-length causes but a small part of the differences between the results of Fajans and Joos and those of Born and Heisenberg, other factors contributing more largely, and as in other cases to be considered the data are often inadequate for extrapolation to infinite wave-length, it seems best in the present paper to use the values for the D-line. Although the differences between the different sets of data are, as a rule, too small to affect the conclusions to be drawn, the following tabulation of the results lays most weight upon the values of Fajans and Joos because they are obtained for the D-line and because these investigators took into account certain complications not provided for by Wasastjerna. The refractions are those which the atoms or ions should have when so isolated as to be practically unaffected by the fields of neighbouring atoms or ions. Table I. gives below the symbol of the atom or ion its refraction for the D-line, and below that the value of f for an electron in the outer shell.

The investigators whose results are shown in Table I. have noted the increase in refraction on passing downward in a column in approximate conformity to the relation observed

* K. Fajans and G. Joos, *Z. Physik*, xxiii. p. 1 (1924).

† J. A. Wasastjerna, *Z. physik. Chem.* ci. p. 193 (1922); *Soc. Scient. Fennica, Commentationes Physico-Math.* i. p. 37 (1923).

by Cuthbertson *, and the decrease in passing along a period from left to right showing increase in constraint with increasing nuclear charge. In the paper already referred to, the writer noted the uniform decrease in f on going from neon to xenon through the family of the rare gases, and from fluorine to iodine in the diatomic molecules of the halogens. In calculating f it was assumed that all the electrons in the outer layer of the atom or those whose orbits extended farthest out from the nucleus were capable

TABLE I.

Ionic Refractions and Values of f.

			He	Li^+		Be^{++}		B^{+++}		C^{++++}
R_D			·50	·20		·09		·05		·03
$f\times10^{-6}$			2·32	5·8		12·9		23·2		38·6
	O^{--}	F^-	Ne	Na^+		Mg^{++}		Al^{+++}		Si^{++++}
R_D	7	2·5	1·00	·50		·29		·17		·1
$f\times10^{-6}$	·66	1·85	4·63	9·27		16·0		27·3		46·3
	S^{--}	Cl^-	A	K^+	Ca^{++}		Sc^{+++}		Ti^{++++}	
R_D	15	8·7	4·20	2·23	1·35	Zn^{++}	·97		·69	
$f\times10^{-6}$	·31	·53	1·10	2·08	3·43	·29	4·78		6·72	
	Se^{--}	Br^-	Kr	Rb^+	Sr^{++}	16·0	Y^{+++}		Zr^{++++}	
R_D	16·3	12·2	6·37	3·6	2·25	Cd^{++}	2·6		2·03	
$f\times10^{-6}$	·28	·38	·73	1·29	2·06	2·44	1·78		2·28	
	Te^{--}	I^-	X	Cs^+	Ba^{++}	1·90	La^{+++}		Ce^{++++}	
R_D	24·4	18·5	10·42	6·3	4·3	Hg^{++}	4·0		3·05	
$f\times10^{-6}$	·19	·25	·445	·74	1·08	5·05	1·16		1·52	
						·92				

† The enclosed column is displaced one line down to show that its figures should not be directly related to those in the adjacent columns.

of suffering displacement and thus contributing to the refraction, the others being too rigidly bound to have an appreciable effect upon the refraction. In the neon and argon atoms the number of displaceable electrons should be eight, and the assumption of eight in krypton and xenon led to the uniformly decreasing values of f already mentioned as compared with the fact that the assumption of eighteen as indicated by the original theory of Langmuir caused a sharp increase in going from argon to krypton followed by a decrease in the value for xenon.

In calculating the values of f in Table I. eight displaceable

* C. Cuthbertson, Trans. Roy. Soc. London, cciv. p. 323 (1905); 'Science Progress,' x. p. 1 (1908). C. Cuthbertson and E. B. R. Prideaux, Trans. Roy. Soc. London, ccv. p. 319 (1905). C. Cuthbertson and E. P. Metcalfe, Trans. Roy. Soc. London, ccvii. p. 135 (1907). S. Smiles, 'The Relation between Chemical Constitution and some Physical Properties,' 1910, p. 245.

electrons are assumed for all but the elements in the first line, which contain but two electrons. The values of f in the first period are lower than those in the second, possibly because of the absence of screening effect in the structures of the first period. No distinction can be made between the electrons of the same total but different azimuthal quantum numbers indicated by the Bohr theory, so that f may be but an average value in the case of most of the ions.

Since Fajans and Joos and Born and Heisenberg, in their papers which came out shortly after the writer's preliminary discussion of the quantity f, have given a detailed treatment of the refractions and deformabilities of the atoms and ions in Table I., discussion of the corresponding values of f appears unnecessary. However, some interesting relations appear when f can be calculated for electrons which form valence bonds between molecules. In the preliminary treatment of the subject f was calculated for the electrons in a number of simple molecules, the results thus obtained being averages of the values for electrons in different parts of the molecules. The work of Fajans and Joos and Born and Heisenberg has shown that the constraint upon an electron in an ion is increased by the proximity of other ions or molecules, particularly if actual combination occurs. This may be illustrated by the comparison in Table II. of the values

TABLE II.*

Molecular Refractions and Values of f for the Halogen and Hydrogen Halides.

	R_D.			$f \times 10^{-6}$.		
X	X^-	HX	X_2	X^-	HX	X_2
F.....	2·5	(1·9)	2·91	1·85	(2·44)	2·79
Cl	8·7	6·68	11·67	·53	·69	·69
Br	12·2	9·14	17·43	·38	·51	·47
I	18·5	13·75	31·97	·25	·34	·25

of R_D and f for the halogen ions with those for the hydrogen halides and the diatomic halogen molecules, the number of displaceable electrons in the latter being taken as fourteen.

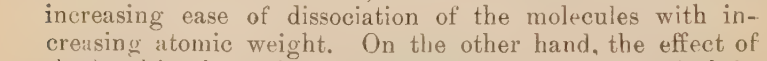
If it could be assumed that the attachment of a hydrogen nucleus to a halogen ion to form a hydrogen halide molecule

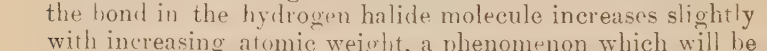
* The values for the ions are taken from Table I., the refraction of hydrogen fluoride is a value estimated by Fajans and Joos, and the other values are calculated from data contained in Landolt-Börnstein, 5th edition.

affected only the two electrons which are supposed to form the valence bond, the contribution to the molecular refraction of the other six electrons in the outer layer would be three-fourths of the ionic refraction, and that of the two binding electrons would be the difference between this and the molecular refraction. In the case of the hydrogen halides, this difference is practically zero, which might seem to indicate that the binding electrons are under such rigid constraints as to be incapable of being appreciably displaced, but in some cases where the bonds must be more rigid the contribution to the refraction of the binding electrons appears to be a negative quantity when calculated in this way, which shows that the electrons other than those forming the bond suffer a loss of mobility, although they are probably less rigidly constrained than the binding electrons. Presumably, all the outer electrons contribute to the molecular refraction in greater or less degree according to their positions in the molecule. The average values of f show that the bond in the fluorine molecule produces a greater decrease in electron mobility than that in the hydrogen fluoride molecule, but, with increasing atomic diameter, the effect of the bond in the halogen molecule diminishes until the electrons in the I_2 molecule are hardly more constrained than those in the I^- ion, which is consistent with the increasing ease of dissociation of the molecules with increasing atomic weight. On the other hand, the effect of the bond in the hydrogen halide molecule increases slightly with increasing atomic weight, a phenomenon which will be discussed presently.

Instead of calculating the average value of f for a number of differently situated electrons in a molecule, it is simpler to consider the contribution of this group of electrons to the molecular refraction. Contributions of this character may be calculated by means of the simple equations used by von Steiger * to calculate bond refractions from atomic refractions and other equations constructed on similar principles, of which the following are given as examples, the first four, which involve only carbon and hydrogen, being those of von Steiger :—

$$(\mathrm{C-H})=1/4\,\mathrm{C}+\mathrm{H};\quad (\mathrm{C-C})=1/2\,\mathrm{C};$$
$$(\mathrm{C=C})=\mathrm{C}+1^{=};\quad (\mathrm{C\equiv C})=3/2\,\mathrm{C}+1^{\equiv};$$





* A. L. von Steiger, *Ber.* liv. p. 1381 (1921).

In these equations, each line joining the atoms represents a bonding electron pair, and each dot a displaceable electron which does not enter into a bond. The refraction, in each case, is supposed to arise only from the electrons thus indicated. H, C, O′, O<, O″, X, $SiCl_4$, and SF_6 represent respectively the atomic or molecular refractions of hydrogen, carbon, hydroxyl oxygen, ethereal oxygen, carbonyl oxygen, a halogen, silicon tetrachloride, and sulphur hexafluoride, and $1^{=}$ and $1^{\equiv}$ are the refractions assigned to the double and the triple bond. The results calculated in this manner are given in Table IV., which shows each electron group with the value of its refraction to the right and a reference to the source of the data used to obtain this value. Whenever possible, use has been made of the average values for the atomic refractions given in well recognized tables, such as those of Eisenlohr *, and when data on individual substances have been employed the reliable results for all available substances have been averaged. As a check upon the results, the refractions of the electron groups may be used to calculate molecular refractions. The results in Table III., which gives some of these calculations for widely differing substances chosen as typical, show that the errors of this method are no greater than those due to experiment and to the minor differences of grouping which are so small as not yet to have been explained.

TABLE III.

Comparison of Calculated and Observed Molecular Refractions (D-line).

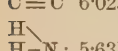
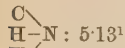
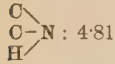
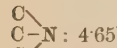
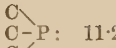
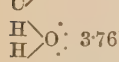
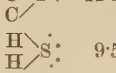
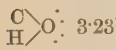
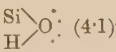
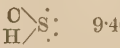
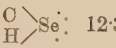
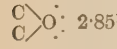
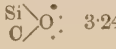
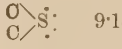
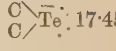
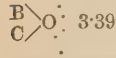
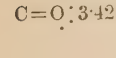
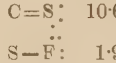
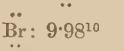
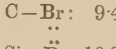
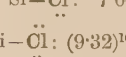
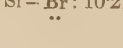
	Calculated.	Observed †.
$n-C_3H_7NH_2$ / $i-C_3H_7NH_2$	$2(C-C)+7(C-H)+\overset{C}{\underset{H}{\overset{\diagdown}{\diagup}}}N\overset{H}{:}=19{\cdot}48$	19·43 / 19·59
C_2H_5OH	$(C-C)+5(C-H)+\overset{C}{\underset{H}{\overset{\diagdown}{\diagup}}}O\overset{\cdot}{:}=12{\cdot}96$	12·78
$n-C_4H_9OH$ / $(CH_3)_3COH$	$3(C-C)+9(C-H)+\overset{C}{\underset{H}{\overset{\diagdown}{\diagup}}}O\overset{\cdot}{:}=22{\cdot}20$	22·14 / 22·22
$(C_2H_5)_2S$	$2(C-C)+10(C-H)+\overset{C}{\underset{C}{\overset{\diagdown}{\diagup}}}S\overset{\cdot}{:}=28{\cdot}65$	28·54
CO_2	$2C=O\overset{\cdot}{:}=6{\cdot}84$	6·71
CS_2	$2C=S\overset{\cdot}{:}=21{\cdot}22$	21·36

† The observed molecular refractions are taken directly from Landolt-Börnstein, 5th edition, or calculated from the refractive indices there given.

* Landolt-Börnstein, 5th edition, p. 985.

Table IV.

Refractions of Electron Groups.

H–H 2·08[1]				
C–H 1·705[1]			C–Zn 4·73[2]	C–Hg 6·91[3]
C–C 1·209[1]		C–Si 2·30[5]	C–Sn 4·02[4]	C–Pb 5·02[4]
C=C 4·15[1]				
C≡C 6·025[1]				
				
				
				
				
				
				
				
				
				
				
				
				

[1] Landolt-Börnstein, 5th edition, pp. 961–985.
[2] A. Ghira, *Gazz. chim. ital.* xxiv. p. 324 (1894).
[3] A. Ghira, *Atti Accad. Lincei*, (5) iii. A. p. 297 (1894).
[4] A. Ghira, *ibid.* p. 332 (1894).
[5] G. Abati, *Z. physik. Chem.* xxv. p. 353 (1898).
[6] F. Eisenlohr, *Spektrochemie Organischer Verbindungen*, pp. 69–72 (1912).
[7] T. S. Price and D. F. Twiss, J. Chem. Soc. ci. p. 1259 (1912).
[8] S. Smiles, 'The Relations between Chemical Constitution and Some Physical Properties.' p. 277 (1910).
[9] G. Pellini and A. Menin, *Gazz. chim. ital.* xxx., II. p. 465 (1900).
[10] K. Fajans and G. Joos, *op. cit.* p. 27.
[11] F. Swarts, *J. chim. phys.* xx. p. 30 (1923). The refractive effect of fluorine varies somewhat with the nature of the molecule containing it, but the value given for C–F: may be regarded as representative.

The values in Table IV. show that the electrons binding two carbon atoms are more tightly held than those binding a carbon and a hydrogen atom, which, in turn, are more tightly held than the two electrons in the hydrogen molecule. If it is assumed, as indicated by the dashes connecting the atomic symbols in the table, that two electrons are shared in the single bond, four in the double, and six in the triple, the actual value of f for each electron in these bonds may be calculated, as well as the values for other bonds listed in Table V.

TABLE V.

Values of f for Bonding Electrons.

	$f \times 10^{-6}$
H—H	·56
C—H	·679
C—C	·958
C=C	·558
C≡C	·576
C—Si	·504

We do not know the distance of the hydrogen nucleus from the electrons in the C—H bond, but it is apparent that the hydrogen exerts less force on these electrons than does the carbon nucleus with its larger charge in the C—C bond. If it is assumed, as seems probable from the results of X-ray analysis, that the outer electrons in the atoms of the diamond have their effective positions located in pairs between the atoms, so that each atom may be treated as sharing a pair of electrons with each of four other atoms, the value of f for these electrons may be calculated from data on the refractive index and density of the diamond given in Landolt-Börnstein (5th edition). The value, $1{\cdot}10 \times 10^6$, is close to the figure, $\cdot 958 \times 10^6$, for the electrons in the C—C bond, but somewhat higher, as might be expected from the fact that the close packing in the diamond lattice probably gives opportunity for a given electron pair to be constrained by the force fields of atoms other than the two between which the pair lies. Although the silicon nucleus has a larger charge than the carbon, its greater distance from the electrons in the C—Si bond causes it to exert a smaller force upon them so that they are more loosely held than the electrons in the C—H bond.

The looser binding of the electrons in the double and triple bonds is in accord with the ease with which addition may occur at these bonds. The slightly greater constraint

upon the electrons of the triple bond is in harmony with the fact that molecules containing this bond show, on the whole, less unsaturation than those containing the double bond, but the difference is too small to be significant. In the light of these relations, it is interesting to examine an hypothesis sometimes advanced to explain the structures of the molecules containing these bonds, namely, that the arrangement of the effective positions of the electrons is such that one pair occupies each apex of a regular tetrahedron, two tetrahedra sharing an apex in the case of a single bond, an edge in the case of a double bond, and a face in the case of a triple bond.

When two tetrahedra share an edge as assumed in the case of the double bond, the positive nuclei, supposed to lie at the centres of the tetrahedra, are brought closer together than in the case of the single bond and consequently repel each other more strongly. This increased repulsion tends to increase the distance between the nuclei, thereby increasing the distance of the nuclei from the bonding electrons at the two shared apices. The mutual repulsion of these two electron pairs acting along the shared edge tends to increase the length of this edge, thereby increasing the distance of the electron pairs from the positive nuclei, but this effect is opposed by the components along the edge of the attractive forces exerted by the positive nuclei. The net result of these effects would probably be an increase in the distance of the binding electrons from the positive nuclei and, as a consequence, the observed decrease in the constraints acting upon the electrons. In the case of the triple bond, the sharing of a face by two tetrahedra should bring the positive nuclei closer together than in the case of the double bond, the repulsion between the two nuclei being correspondingly greater. The repulsion between the electron pairs at the three shared apices should be greater because each pair would be acted upon by the resultant of the repulsive forces exerted by the other two pairs. Since the positive nuclei should be closer to the plane in which these forces act, the components in this plane of the attractive forces which they exert upon the electrons should afford greater opposition to the moving apart of the electron pairs than in the case of the double bond, but this increase in the attractive force should not be sufficient to balance the increase in the tendency of the electron pairs to move apart because of their mutual repulsion. One would, therefore, predict somewhat weaker constraints on the electrons in the triple bond than in the double, while the values of f show the

electrons of the triple bond to be, if anything, a little more tightly held. The hypothesis of two tetrahedra sharing an edge in a double bond and a face in a triple bond gives a satisfactory explanation of the smaller electron constraint in these bonds as compared to that in the single bond, but fails to explain the almost equal constraints in the double and triple bonds, although the difference demanded by the hypothesis is not necessarily great and the failure may be due to the difficulty of taking proper account of all the variables. If this problem were considered from the ordinary point of view of atomic refractions, the greater refraction assigned to the triple bond would lead to the expectation of greater unsaturation and greater readiness to take part in addition reactions than in the case of the double bond.

The value of f, $\cdot 245 \times 10^6$, calculated for the electron pair of the C—Zn bond, shows the decrease of the electron constraint with increase in atomic diameter. The refraction, 4·73, calculated for this electron pair from the refractive indices of zinc methyl and zinc ethyl presumably contains a small contribution from the completed shell of electrons underlying the bonding pairs, as Table I. shows a value of ·29 for the refraction of the ion Zn^{++}, which must, however, be considerably decreased by the proximity of the other atoms in the zinc methyl and zinc ethyl molecules. The refraction, 6·91, calculated for the C—Hg bond from data on mercury dimethyl and mercury diethyl, contains a considerable contribution from the underlying shell of electrons in the mercury atom. If these electrons were unaffected by the other atoms in the molecule, this contribution would be one-half of the refraction of the Hg^{++} ion shown in Table I., or 2·53, but it is undoubtedly reduced by the fields of the other atoms in the molecule. If the value assigned to the C—Hg bond is doubled, the resulting figure, 13·82, is the refraction due to the two pairs of binding electrons together with that due to the underlying electron shell. This figure is close to the value, 13·94, calculated from data in Landolt-Börnstein and given by Fajans and Joos* for the atomic refraction of mercury vapour, the atoms of which contain two unshared valence electrons. The refractions of the C—Sn and C—Pb bonding pairs, which presumably contain contributions from the first underlying electron shells, show the usual decrease in electron constraint with increase in atomic size.

The rest of the refractions shown in the table are for

* *Op. cit.* p. 35.

groups of eight electrons, one, two, or three pairs of which serve as bonds between atoms. The shell underlying this group of eight electrons can make no appreciable contribution to the refraction. The values for the $Ti-\ddot{\underset{\cdot\cdot}{Cl}}:$ and $Sn-\ddot{\underset{\cdot\cdot}{Cl}}:$ groups, the first of which loses somewhat in significance because of strong dispersion, presumably contain very small contributions from the underlying electron shells in the titanium and tin atoms, but contributions of this character should be negligible in the other groups.

In the values for the nitrogen electron group, calculated from data on ammonia and the amines, it is apparent that an attached carbon atom causes greater electron constraint than a hydrogen, the constraint increasing from the $\begin{matrix}H\\ \diagdown\\ H-N:\\ \diagup\\ H\end{matrix}$ to the $\begin{matrix}C\\ \diagdown\\ C-N:\\ \diagup\\ C\end{matrix}$ group. The difference in effect is less marked in the larger phosphorus electron group. Similarly, the carbon atom produces stronger constraint than the hydrogen when attached to an electron group of the oxygen family, but the difference in effect decreases as the volume of the group increases with accompanying decrease in the electron constraint. When a carbon atom attached to the group $\begin{matrix}C\\ \diagdown\\ C\diagup O:\end{matrix}$ is replaced by the larger atom of silicon, the electron constraint is decreased, and when the remaining carbon is replaced by a hydrogen to give the group $\begin{matrix}Si\\ \diagdown\\ H\diagup O:\end{matrix}$ a further decrease in the electron constraint is apparent, although the value of the refraction is somewhat uncertain because of the fact that it was obtained from measurements upon a solution of silicic acid. When a carbon atom is replaced by a boron atom with its smaller nuclear charge, a considerable decrease in the electron constraint is apparent, and the weaker forces exerted by the boron nucleus are evident again in the higher values for the refractions of the $B-\ddot{\underset{\cdot\cdot}{Cl}}:$ and $B-\ddot{\underset{\cdot\cdot}{Br}}:$ groups as compared with those for the $C-\ddot{\underset{\cdot\cdot}{Cl}}:$ and $C-\ddot{\underset{\cdot\cdot}{Br}}:$ groups. The relative effects of the carbon and hydrogen atoms in increasing the electron constraint is shown again by comparison of the refractions for the $C-\ddot{\underset{\cdot\cdot}{X}}:$ group with those for the $H-\ddot{\underset{\cdot\cdot}{X}}:$ group in Table II. A carbon atom

attached to a fluorine group produces greater electron constraint than a hydrogen, the difference in the effects is smaller for the chlorine group, and, in the bromine and iodine groups, the attached carbon actually produces smaller constraint than a hydrogen. It is thus generally observed that, with increasing size of the electron group the difference between the effect of an attached hydrogen and that of an attached carbon becomes relatively smaller and may even reverse its sign. This may be explained by supposing that the carbon nucleus with its two electrons in the inner shell or K-level does not greatly alter its distance from the bonding electron pair as the volume of the electron group to which it is attached increases, but that the hydrogen nucleus approaches more closely to the bonding electron pair as the increasing distance of this pair from the nucleus of the electron group makes possible such an approach because of the decreasing repulsion of the two nuclei. Such an approach might actually extend to a penetration of the outer electron shell by the hydrogen nucleus, as suggested by certain investigators in the case of the hydrogen halides *. This approach would increase the force exerted by the hydrogen nucleus on the electrons as compared with that exerted by the carbon nucleus, thus causing the effect noted. It is apparent that the forces exerted upon the electrons in a group decrease as the volume of the group increases, and increase as the nuclear charge of an atom increases without increase in volume, as is the case in a horizontal period of the Periodic System.

In an attempt to determine the effect of a hydrogen nucleus attached to one atom in a molecule upon the electrons in the adjacent atoms of the molecule, the value for $C-\ddot{\underset{\ddot{}}{X}}:$ was calculated from the molecular refraction of a large number of halogen-substituted hydrocarbons, particular attention being paid to isomers. A number of cases were found in which a nearby hydrogen nucleus appeared to increase slightly the constraint upon a chlorine electron, and none in which it caused a decrease, but, as the differences noted were small, and as nothing definite could be drawn from the very limited data available for testing the other halogen compounds, the results were regarded as inconclusive.

The strong forces acting in the fluorine structure are

* H. Bell, Phil. Mag. xlvii. p. 549 (1924). M. Born and W. Heisenberg, *op. cit.*

shown by the results of Swarts * for unsaturated fluorine substitution products. The replacement of a hydrogen by a fluorine atom in a saturated compound ordinarily causes a decrease in the molecular refraction of about 0·1, while a similar substitution at an unsaturated carbon causes a decrease of 0·2 to 0·6, presumably, because the fluorine structure tightens the constraint upon the loosely held electrons of the unsaturated bond.

Comparison of the refractions for the $C=\dot{O}:$ and $C=\dot{S}:$ groups with those for the $\begin{matrix}C\diagdown\\C\diagup\end{matrix}\dot{O}:$ and $\begin{matrix}C\diagdown\\C\diagup\end{matrix}\dot{S}:$ groups shows the smaller constraint of the electrons in the double bonds. The exaltation of the refraction in a conjugated system gives evidence of a loosening of the constraint upon the electrons in the neighbourhood of those in the double bonds, but the actual mechanism of this decrease in constraint cannot be clear until the phenomena of the double and triple bonds are better understood.

The refractions calculated for the electron groups in the hexafluorides of sulphur, selenium, and tellurium show an interesting progression. The value for $S-\ddot{F}:$, 1·95, is larger than the value for $C-\ddot{F}:$, 1·60, by no more than might be expected because of the larger size and hence lower electron constraint in the sulphur atom, while the value for $Te-\ddot{F}:$ differs by a negligible amount from the refraction given for the fluoride ion in Table I. The group $Te-\ddot{F}:$ would seem to be practically identical with the fluoride ion, although the stability and low boiling-point of tellurium hexafluoride are properties not ordinarily associated with substances whose molecules contain polar bonds. As the carbon-fluorine bond is one which would ordinarily be classed as non-polar, the electron groups under consideration apparently show a gradual transition from a polar to a non-polar type of linkage. One might regard the sulphur-fluorine bonds in sulphur hexafluoride as polar and consider that the refraction of the $S-\ddot{F}:$ group is diminished by the attractive forces exerted by the sulphur nucleus, which does not differ materially from the situation existing if the bonds are non-polar. If the bonds are polar, we have fluoride ions

* F. Swarts, *op. cit.*

arranging themselves more or less symmetrically about the central structure but somewhat deformed by the forces exerted by this structure. If the bonds are non-polar, we have an electron pair shared between each fluorine group and the central structure, but the location of these shared pairs may be identical with that which they would occupy in the case of the so-called polar linking, so that the distinction between the polar and the non-polar bond in molecules of this character is seen to be one merely of nomenclature.

A similar argument applies to the increase in refraction from $C-\ddot{\underset{\cdot\cdot}{Cl}}:$ through $Si-\ddot{\underset{\cdot\cdot}{Cl}}:$ to $Sn-\ddot{\underset{\cdot\cdot}{Cl}}:$, the value for which is only slightly lower than that given for the chloride ion in Table I.

Summary.

The forces opposing the displacement of the outer electrons in ions and molecules are calculated from the refractions. When the force cannot be calculated for an individual electron, the contribution to the refraction of a group of electrons is taken as an inverse measure of the average force acting upon these electrons. It is found that, where unsaturation exists, the constraint upon the electrons is low and that, in general, the forces exerted upon electrons shared between atoms, as well as those acting upon the unshared outer electrons of atoms or ions, decrease as the number of underlying electron shells increase and increase when the nuclear charge increases without increase in the number of underlying shells.

Princeton, New Jersey, U.S.A.
November 1, 1924.

XXXVI. *Multiplet Structure.* *By* Arthur Bramley, *Ph.D.*, *Fellow in Physics, Princeton University* *.

THE equations of motion of an electron, describing a path about a central charge, without radiation of energy, can be written in the form

$$\frac{d^2x^i}{ds^2} + \Gamma^i_{\alpha\beta}\frac{dx^\alpha}{ds}\frac{dx^\beta}{ds} = 0,$$

where the Γ's are sets of functions depending on the position of the charge and electron.

* Communicated by the Author.

The general quadratic solution of the above set of equations is of the form

$$e^{\int \phi_\alpha dx^\alpha}\left[g_{ij}\frac{dx^i}{ds}\frac{dx^j}{ds}\right] = \text{const.},$$

where the ϕ_α is a vector which becomes in the above case the momentum of the moving charge in the x^α direction, and g_{ij} is a tensor of the second order *.

If the solution is periodic, then

$$\int p_\alpha dx^\alpha = n\kappa,$$
$$\kappa = \text{const.},$$
$$p_\alpha = \text{momentum in the } x^\alpha \text{ direction.}$$

The relative invariant integral

$$\int p_\alpha dx^\alpha$$

is equal to the absolute invariant integral

$$\iint \delta p_\alpha \delta x^\alpha,$$

where each double integral is taken over the projection of the section of the tube of paths on the corresponding $p_\kappa q_\kappa$ plane. The integral

$$\iint \delta p_\alpha \delta x^\alpha = n\kappa$$

can be reduced to a system of one degree of freedom invariantly so that we get

$$\int p_\alpha dx^\alpha = n\kappa,$$
$$\alpha \text{ not summed.}$$

This gives the familiar quantum integrals for the three spatial components, but in addition it leads to the quantization of the time momentum

$$\int p_4 dt = n\kappa,$$

which is a necessary consequence of the idea that the spatial and time directions have equal significance.

The above argument has been given for the three spatial components by E. P. Adams ('Quantum Theory,' p. 38). The considerations outlined above lead to the conclusion that only tubes of paths can exist in the four-dimensional manifold which are multiples of unit tubes.

The fundamental quadratic form associated with the motion of an electron about a central charge E is

* Eisenhart, Trans. of A. M. S., July 1924.

$$H = 2m\left[\left(\frac{dr}{ds}\right)^2 + r^2\left(\frac{d\theta}{ds}\right)^2 + r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)^2\right] - \left(1-\frac{eE}{r}\right)\left(\frac{dt}{ds}\right)^2,$$

where

H = energy of the electron,
m = mass of the electron,
e = charge on the electron ;

or

$$H\left[1+\frac{1}{H}\left(\frac{dt}{ds}\right)^2\right] = 2m\left[\left(\frac{dr}{ds}\right)^2 + r^2\left(\frac{d\theta}{ds}\right)^2 + r^2\sin^2\theta\left(\frac{d\phi}{ds}\right)^2\right] + \frac{eE}{r}\left(\frac{dt}{ds}\right)^2.$$

If we consider the spatial quantum integral, *e. g.*

$$\int g_{11}\left(\frac{dr}{ds}\right)dr = \kappa n,$$

then we have

$$\int 2m\left(\frac{dt}{ds}\right)\left(\frac{dr}{dt}\right)dr = \kappa n,$$

but

$$m\left(\frac{dt}{ds}\right) = m_0,$$

the invariant mass of the electron, and our invariant integral becomes

$$2m_0\int\left(\frac{dr}{dt}\right)dr = \kappa n,$$

the familiar law where

$$\kappa = h = \text{Planck's constant.}$$

Considering next the time component, we have

$$\int g_{44}\frac{dt}{ds}\,dt = hn,$$

or

$$\int\left(1-\frac{eE}{r}\right)\left(\frac{dt}{ds}\right)^2 ds = hn.$$

But from the integral of the equation of motion,

$$\frac{d^2t}{ds^2} + \frac{d}{dr}(\log g_{44})\frac{dr}{ds}\frac{dt}{ds} = 0,$$

we have

$$g_{44}\left(\frac{dt}{ds}\right) = \text{const.},$$

which is analogous to the equation of areas,

$$g_{22}\left(\frac{d\theta}{ds}\right) = \text{const.}^*$$

Hence our time invariant integral becomes

$$\int\left(g_{44}\frac{dt}{ds}\right)^2\frac{ds}{g_{44}} = \left(g_{44}\frac{dt}{ds}\right)^2\int\frac{ds}{g_{44}} = nh.$$

To a first approximation we have

$$\left(g_{44}\frac{dt}{ds}\right)^2\frac{\mathrm{S}}{g_{44}} = nh,$$

where S is the length of the periodic path.

Since S corresponds to the measured time in experimental observations, we have

$$\left(\frac{dt}{ds}\right)^2 = \frac{nh}{g_{44}\mathrm{T}},$$

$$\mathrm{T} = \text{periodic time.}$$

From the solution of the spatial components of momentum integral we have

$$\mathrm{H}\left[1+\frac{\left(\frac{dt}{ds}\right)^2}{\mathrm{H}}\right] = \frac{2\pi^2 m\mathrm{E}^2e^2}{n_1{}^2h^2},$$

$$n_1 = \text{total quantum number,}$$

or

$$\mathrm{H} = \frac{2\pi^2 m\mathrm{E}^2e^2}{n_1{}^2h^2}\left[1-\frac{hn}{g_{44}\,.\,\mathrm{H}\,.\,\mathrm{T}}\right].$$

Moreover, since

$$g_{44} = 1-\frac{e\mathrm{E}}{r},$$

we have to a first approximation, since

$$g_{44} = 1-\tfrac{1}{2}\mathrm{H} \quad \text{on the average,}$$

$$\mathrm{H} = \frac{2\pi^2 m\mathrm{E}^2e^2}{n_1{}^2h^2}\left[1-\frac{\gamma n}{hn_1}\right],$$

for

$$\mathrm{HT} = \left(2\pi^2\frac{\mathrm{M}m}{\mathrm{M}+m}\frac{\mathrm{E}^2e^2}{n_1{}^2h^2}\right)\left(\frac{1}{4\pi^2}\frac{\mathrm{M}+m}{\mathrm{M}m}\frac{n_1{}^3h^3}{\mathrm{E}^2e^2}\right) = \tfrac{1}{2}n_1h,$$

using the values of H and T derived for the simple atom

* Eddington, Math. Th. of Rel. p. 86.

and where γ is a constant which is introduced from the change in the units of T. Therefore

$$H = W[1-\gamma' . W^{1/2} . n] = \text{energy of the electronic orbit,}$$

where

$$W = \frac{2\pi^2 M E^2 e^2}{n_1^2 h^2} = \text{the highest energy level of the multiplet,}$$

and

$$\gamma' = \gamma(2\pi^2 m E^2 e^2)^{-1/2}.$$

The constant γ cannot, however, be determined accurately owing to the indeterminateness of the scalar gauge vector in the quadratic first integral which is determined from the electromagnetic field.

If ν and ν' are the frequencies of two lines of a multiplet arising from the same initial state (or ending in the same final state), then

$$h\nu = H_1 - H_2,$$

$$h\nu' = H_1 - H_2';$$

$$\therefore \quad \nu - \nu' = \frac{1}{h}[H_2' - H_2] = \gamma'(n-n')W_2^{3/2}$$

= frequency difference of two lines of a multiplet where H_2 and H_2' have the same n_1, but different n's.

Thus the frequency separations of the components of the lines of a spectral series of any particular element should vary as $W^{3/2}$, where W represents the highest energy level of the components of the multiplet. Further, the ratio of the frequency separations of the components of any one multiplet should be as the ratio of simple integers, *e. g.* in the triplets of the principal series this ratio is *two*.

Since the values of W for the energy of any one particular level in the optical series for any set of similar chemical elements is nearly constant, the frequency separations of the components of any multiplet should vary as γ' from one element to another similar element. Now the constant γ' should vary as N^2, where N represents the atomic number of the element, so that the frequency difference of the energy levels of similar chemical elements varies as N^2, according to the law which was first stated by Dunz (Sommerfeld, *Atombau u. Spektrallinien*, p. 454).

The case of the fine structure of the H and He atoms as well as that of the X-ray spectra considered by Sommerfeld is a degenerate case of the above considerations where s and t become identical. In this case the space degenerates into a

three-dimensional spatial manifold and the invariant integrals become the usual quantized action integrals. The theory outlined above applies, on the other hand, only to the optical spectra of the elements with more than one electron, since the constant γ depends on the dynamical properties of the inner core, *i. e.* on the nucleus and the inner electrons. The introduction of the "inner quantum number" n arises through the rotational motion of this inner core with respect to the observer.

The following table contains the computed and experimental frequency differences for the energy levels of the spectra of typical alkaline earth and metals, using the 3/2 power law. The data are taken from the tables in Fowler's Report on Series in Line Spectra. The energy levels of the spectra of the other elements of these families has been computed and compared with the experimental results, the agreement being of the same accuracy except in the case of Ba (non-ionized) which, however, is non-Ritzean in type.

Potassium.

State.	$\Delta\nu$ exp.	$\Delta\nu$ calc.
$m\pi$		
21963·06		
22020·77	57·71	
10285·70		
304·39	18·69	18·29
6001·18		
9·33	8·15	8·32
3930·00		
4·83	4·83	4·34
2778·27		
80·56	2·29	2·86

Calcium (ionized).

$m\delta$		
82089·32		
28·73	60·85	
38900·47		
881·30	19·19	19·8
23017·56		
8·95	8·61	9·0

Calcium.

State.	$\Delta\nu$ exp.	$\Delta\nu$ calc.	
mp			
33988·7			
4094·6	105·9		
146·9	52·2		
12730·3			
50·2	19·9	19·1	
			Only the larger separation is calculated, the other component being, according to the theory, a simple fraction of this.
6777·8			
85·6	7·8	7·7	
89·6	4·0		
md			
28969·1			
55·2	13·3		
33·5	22·2		
11556·4			
52·6	3·7		
47·0	5·6	5·6	
6561·4			
59·7	1·7		
56·9	2·8	2·4	
4255·5			
54·0	1·4		
2·2	1·8	1·4	

In conclusion, the writer wishes to express his gratitude to Professor E. P. Adams for his interest and assistance during the writing of this paper, which is a continuation of the paper on "The Motion of an Electric Charge"*.

XXXVII. *On Certain Postulates of the Quantum Theory.* *By* Dr. D. N. Mallik, *Professor of Physics, Muslim University, Aligarh, India* †.

Summary.

FROM Langrange's equations in generalized coordinates, the general quantum condition is deduced in the form $\int E\,dt = Nh$ (where E is the energy of a radiating system and N an integer, h being Planck's constant).

Taking this as the fundamental postulate of the Quantum theory, Fermat's law of swiftest propagation of light and

* Phil. Mag. May 1925, p. 912.

† Communicated by the Author.

Planck's postulate regarding the equality between the frequency in a stationary orbit and that of subsequent radiation are deduced.

It is then shown that this equality may be explained as well as the Zeeman and Stark effects by considering the motion as that in a disturbed circular orbit. This suggests a concordance between the Quantum theory and the ordinary wave-theory points of view.

It is then pointed out that both theories fix attention on the mean value of the energy of radiation which can also be shown, on the ordinary Electron theory, to be proportional in some cases at least to the frequency as postulated in the Quantum theory.

1. From Langrange's equations in generalized coordinates, if T, V are the kinetic and potential energies and p's the generalized principal coordinates, we have

$$\Sigma\left(\frac{d}{dt}\frac{\partial \mathrm{T}}{\partial \dot{p}} - \frac{\partial \mathrm{T}}{\partial p} + \frac{\partial \mathrm{V}}{\partial p}\right)dp = 0. \quad . \quad . \quad . \quad (1)$$

Multiplying this by dt throughout and integrating with respect to t, we derive, provided we can admit that the order of integration is indifferent,

$$\int \Sigma \frac{\partial \mathrm{T}}{\partial \dot{p}}\, dp + \int \Sigma \frac{\partial (\mathrm{T}-\mathrm{V})}{\partial \dot{p}}\Big) dp/dt = \text{const.} \quad . \quad . \quad (2)$$

This yields equations of the type

$$\int \frac{\partial \mathrm{T}}{\partial \dot{p}}\, dp = \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

since p's are independent, admitting

$$\Sigma \int \frac{\partial}{\partial p}(\mathrm{T}-\mathrm{V})dp\, dt = \delta \int (\mathrm{T}-\mathrm{V})dt = 0. \quad . \quad . \quad (4)$$

This seems to be reasonable, since the initial and final configurations being prescribed, there is nothing to distinguish, during the integration, between the present operator ∂ and the operator δ of the calculus of variation. In any case, the left-hand side is zero for a closed orbit.

Now in accordance with quantum ideas, we may evidently take (subject to the limitations specified above)

$$\int \frac{\partial \mathrm{T}}{\partial \dot{p}}\, dp = n_p h \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where n_p is an integer and h is Planck's constant, showing the exact relation between classical and quantum dynamics.

2. Again if E is the total energy of the system

$$2\int \mathrm{E}dt = \int \Sigma\left(\frac{\partial \mathrm{T}}{\partial \dot{p}}\dot{p} + \int \frac{\partial \mathrm{V}}{\partial p}dp\right)dt = \int \Sigma \frac{\partial \mathrm{T}}{\partial \dot{p}}dp + \int \Sigma \mathrm{F}_p\, dp$$

$$= \Sigma \int \frac{\partial \mathrm{T}}{\partial \dot{p}}dp \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

if $\Sigma \int \mathrm{F}_p\, dp = 0$, F_p being the impulse corresponding to p.

This, of course, would be true whenever the displacement is zero while the impulse acts.

Assuming this as a condition in the postulation of quantum theory, we get

$$\int \mathrm{E}dt = \mathrm{N}h \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

from (5) and (6), where N is an integer, since fractional values of the coefficient of h are excluded.

3. It should be noted that equation (3) admits of direct verification in the case of the Bohr model of the hydrogen atom. For this (in three dimensional motion) let

$x, y, z,$ be the cartesian coordinates of the electron,
X, Y, Z those of the nucleus,
r, θ, ϕ polar coordinates of the electron,
R, θ, ϕ polar coordinates of the nucleus.
m, M, the masses of the electron and the nucleus.

$$\therefore \qquad 2\mathrm{T} = (m\dot{x}^2 + \mathrm{M}\dot{\mathrm{X}}^2) + \; + = m\dot{x}(\dot{x} + \dot{\mathrm{X}}) + \; \ldots,$$

since $mx = \mathrm{M}\mathrm{X}^x$, etc.

Hence the equation corresponding to (2) becomes

$$\int\left(\frac{\partial \mathrm{T}}{\partial \dot{x}}dx + \frac{\partial \mathrm{T}}{\partial \dot{y}}dy + \frac{\partial \mathrm{T}}{\partial \dot{z}}dz\right) + \int\left(\frac{\partial \mathrm{T}}{\partial \dot{\mathrm{X}}}\partial \mathrm{X} + \frac{\partial \mathrm{T}}{\partial \dot{\mathrm{Y}}}d\mathrm{Y} + \frac{\partial \mathrm{T}}{\partial \dot{\mathrm{Z}}}d\mathrm{Z}\right)$$

$$= \int(m\dot{x}\, dx + \mathrm{M}\dot{\mathrm{X}}\, d\mathrm{X}) + \; + \ldots$$

$$= \int(m\dot{r}\, dr + \mathrm{M}\dot{\mathrm{R}}\, d\mathrm{R}) + \int(mr^2 + \mathrm{M}\mathrm{R}^2)\dot{\theta}\, d\theta$$

$$+ \int(mr^2 + \mathrm{M}\mathrm{R}^2)\sin^2\theta\dot{\phi}\, d\phi \quad = \text{constant (8) from (2).}$$

But the last two terms are each of them constant on the principle of angular momentum: therefore from (8), we have

$$\int(m\dot{r}\, dr + \mathrm{M}\dot{\mathrm{R}}\, d\mathrm{R}) = \int \mu\dot{\rho}\, d\rho = \text{const.} = n_3 h \text{ say}, \quad . \quad . \quad . \quad . \quad (9)$$

where

$$\frac{r}{1/m} = \frac{\mathrm{R}}{1/\mathrm{M}} = \frac{\rho}{1/\mu}.$$

And we have the spacial quantum conditions of Sommerfeld.

4. Accordingly the postulate which serves as the basis of the Quantum theory may be stated in the form $\int \mathrm{E}\, dt = \mathrm{N}h$, E being the total energy at any time t.

We have, in fact,

$$\int \mathrm{E}\, dt = \Sigma \mathrm{E}_r t_r, \quad \ldots\ldots \quad (10)$$

where t = period of the rth radiation, if

$$\mathrm{E}_r = h\nu_r = \frac{h}{t_r} \quad \ldots\ldots \quad (11)$$

in accordance with the quantum theory, E_r being the energy given out during the rth radiation.

5. If this is postulated, the minimum increment (Δ) of $\int \mathrm{E}\, dt$,

$$i.e. \qquad \{\Delta \int \mathrm{E}\, dt\}_{\text{min.}} = h, \quad \ldots\ldots \quad (12)$$

on the understanding, however, that for a permanently stable configuration or orbital motion

$$\Delta \int \mathrm{E}\, dt = 0, \quad \ldots\ldots \quad (13)$$

since E = const., and $\int dt$ = const.

6. Again if Δ is replaced in (13) by δ, where δ is the operator of the calculus of variation, we get $\delta \int \mathrm{E}\, dt$ or $\delta \int dt = 0$ (since E is constant in a ray of light during its transmission) which is Fermat's law.

7. If Δ refers to two stationary orbits of a Bohr atom, we shall have also from (12)

$$(\mathrm{E} - \mathrm{E}')\mathrm{T} = h \text{ or } \kappa h, \quad \ldots\ldots \quad (14)$$

where κ is an integer, if during a complete period T, h/T or $\kappa h/\mathrm{T}$ quanta of energy are given out ; or

$$(\mathrm{E} - \mathrm{E}') = \kappa h\varpi \text{ or } h\varpi, \quad \ldots\ldots \quad (15)$$

from (14) where ϖ is the frequency in either of the orbits.

8. But if Δ refers to emission of radiation during a complete period of a vibratory system of simple period $1/\nu$ we have, from (12)

$$\mathrm{E} - \mathrm{E}' = h\nu, \quad \ldots\ldots \quad (16)$$

which is a postulate of the quantum theory of spectral emission.

9. If, then, radiation is associated with change from one stationary orbit to another, we have from (15) and (16).

$$\varpi = \nu \quad \text{or} \quad \kappa\varpi = \nu. \quad \ldots\ldots, \quad (17)$$

Thus the equation $\kappa\varpi = \nu$ ($\kappa = 1, 2 \ldots$) seems to be deducible from general considerations alone.

10. The following analysis suggests a further explanation of this equality.

Consider the motion of a particle in a central orbit. The equations of motion are

$$r - r\dot{\theta}^2 = -\lambda/r^2 . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and

$$\frac{1}{r}\frac{d}{dt}(r^2\dot{\theta}) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Where $\lambda = e^2\left(\frac{1}{m} + \frac{1}{M}\right)$ for hydrogen atom (Bohr model).

Let the orbit be slightly disturbed according to the scheme

$$r = r_0 + \mathrm{R}, \quad \dot{\theta} = \omega + \Omega ;$$

we have then for the equation of small oscillation

$$\ddot{\mathrm{R}} - \mathrm{R}\omega^2 - 2r_0\omega\Omega = \frac{2\mu}{r_0^3}\mathrm{R} \quad . \quad . \quad . \quad . \quad (20)$$

from (18), and

$$\frac{d}{dt}(2r_0\omega\mathrm{R} + r_0^2\Omega) = 0 \quad . \quad . \quad . \quad . \quad . \quad (21)$$

from (19).

For a circular orbit, $r_0 = \text{const.}$, $\omega = \text{const.}$, $r_0\omega^2 = \frac{\mu}{r_0^2}$; whence substituting we get, since R and Ω vanish together,

$$\ddot{\mathrm{R}} + \omega^2\mathrm{R} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Taking $\mathrm{R} \propto \cos pt$ we have $p = \pm\omega$, showing that $\nu = \varpi$ or the frequency of radiation is equal to the frequency of orbital motion, if radiation is due to the harmonic motion set up in the disturbed central orbit.

11. Comparing this with Bohr's theory we gather that a change from one stationary orbit to another is associated with vibratory motion and consequent emission of radiation, so that although the net result is expressible by the equation

$$\mathrm{E} - \mathrm{E}' = h\nu,$$

the result is attained through oscillation of period $1/\nu$.

12. It is worthy of note that the present analysis gives also the Zeeman and Stark effects.

13. Thus for the Zeeman effect, the corresponding equations of the disturbed orbit will be

$$\ddot{\mathrm{R}} - \mathrm{R}\omega^2 - 2r_0\omega\Omega = \frac{2\lambda}{r_0^3}\mathrm{R} + \frac{\mathrm{H}}{\mu}\frac{e}{c}(r_0\Omega + \omega\mathrm{R}) \quad (23)$$

$$\frac{1}{r_0}\frac{d}{dt}(r_0^2\Omega + 2\omega r_0\mathrm{R}) = -\frac{\mathrm{H}\epsilon}{\mu c}\dot{\mathrm{R}}, \quad . \quad . \quad . \quad (24)$$

where e is expressed in electrostatic units, $\frac{1}{\mu}=\frac{1}{m}+\frac{1}{M}$, c=velocity of light, H being perpendicular to the plane of the orbit.

Hence from (24)

$$r_0\dot{\Omega}+\left(2\omega+\frac{He}{\mu c}\right)\dot{R}=0,$$

or
$$r_0\Omega+\left(2\omega+\frac{He}{\mu c}\right)R=0, \quad . \quad . \quad . \quad . \quad (25)$$

since Ω and R vanish together.

Remembering that for undisturbed orbit,

$$r_0\omega^2=\frac{\lambda}{r_0^2}-\frac{He}{\mu c}r_0\omega,$$

this leads to the equation

$$\ddot{R}+\left(\omega^2+\omega\frac{He}{\mu c}\right)R=0, \quad . \quad . \quad . \quad . \quad (26)$$

from (23) and (25), or if

$$R\propto\cos pt,$$

$$p=\pm\omega\pm\frac{1}{2}\frac{He}{\mu c},$$

i. e., if $\Delta\nu$= frequency corresponding to the Zeeman effect

$$\Delta\nu=\pm\frac{1}{4\pi}\frac{He}{\mu c},$$

and $\Delta\nu=0$, when H is in the plane of the orbit.

16. Similarly for the Stark effect the equations of small motion are

$$\ddot{R}-R\omega^2-2\omega r_0\Omega=\frac{2\lambda}{r_0^3}R+\frac{eF}{\mu}\frac{R_0}{r_0}\cos\theta, \quad . \quad . \quad (28)$$

and
$$\left[\frac{1}{r_0}\frac{d}{dt}(r^2\dot{\theta})\right]_{\substack{r=r_0+R\\ \dot{\theta}=\omega+\Omega}}=-\frac{eF}{\mu r_0}R_0\sin\theta, \quad . \quad . \quad . \quad . \quad (29)$$

where F is the electromotive intensity of the exciting field and

$$R=R_0\cos(pt+\alpha),$$
$$\equiv R_0\cos\theta,$$

observing that the radial resolved part of $\frac{Fe}{\mu}$ (which is in the direction of x)$=\frac{eF}{\mu}\cdot\frac{x}{r}$, during finite (steady) motion

and accordingly for disturbed motion the effective part of this is

$$\frac{\mathrm{F}e}{\mu}\frac{\mathrm{R}_0}{r_0}\cos\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

Similarly for the other component.

From the second equation (29) on integrating (since $\dot{\theta}=\omega$ in the small terms) we have

$$\frac{1}{r_0}\Big[r^2\dot{\theta}\Big]_{\substack{r=r_0+\mathrm{R}\\ \dot{\theta}=\omega+\Omega}}=\frac{e\mathrm{F}}{\mu r_0}\frac{\mathrm{R}_0}{\omega}\cos\theta+(r_0\omega), \quad . \quad . \quad . \quad (30)$$

$$\therefore \qquad \frac{1}{r_0}\left[2r_0\mathrm{R}\omega+r_0^2\Omega\right]=\frac{e\mathrm{F}}{\mu r_0}\frac{\mathrm{R}_0}{\omega}\cos\theta. \quad . \quad . \quad (31)$$

Hence, ultimately, we have

$$\ddot{\mathrm{R}}+\omega^2\mathrm{R}=\frac{3\mathrm{F}e}{\mu r_0}\mathrm{R}_0\cos\theta. \quad . \quad . \quad . \quad . \quad (32)$$

from (28) and (31).

$$\therefore \qquad -p^2+\omega^2=\frac{3\mathrm{F}e}{\mu r_0}.$$

$\therefore$ if $\Delta\nu=$ frequency corresponding to the Stark effect

$$\Delta\nu=\pm\frac{3}{4\pi}\frac{\mathrm{F}e}{\mu r_0\omega}, \quad . \quad . \quad . \quad . \quad . \quad (33)$$

where $1/\mu=$sum of the reciprocals of the masses of the electron and the nucleus.

14. We are accordingly justified in concluding that when the motion of an electron is changed by the requisite impulse, oscillations are set up, resulting in emission of radiation of the same frequency (on the simplest supposition at any rate) as that of the steady orbital motion. Since the oscillation is associated with radiation of energy, the orbital path gradually changes and the final configuration is again one of steady orbital motion in a new orbit, as postulated in Bohr's theory.

15. Thus the quantum theory by no means precludes the supposition that the transfer of energy actually takes place [by quanta] through the mechanism of vibrations set up as in the wave theory. This is also practically the conclusion otherwise arrived at by Sommerfeld (p. 263, 'Atomic Structure and Spectral lines').

16. Again, writing the equation (12) in the form

$$\Delta\int\frac{\mathrm{E}dt}{\mathrm{T}}=\frac{h}{\mathrm{T}}=h\nu. \quad . \quad . \quad . \quad . \quad . \quad (34)$$

and remembering that the left-hand side is the mean value of the energy radiated away during a complete oscillation (of period T) we observe that if Δ refers to this condition, the above amounts to the statement that

$h\nu$ = mean value of the energy radiated away during a complete oscillation.

17. The physical meaning of this is that on either theory we can only certainly tell what happens at the initial and final stages of the process of radiation, and also what the mean value of the effect is. For it will be recalled that the explanation of even the phenomena of diffraction on the undulatory theory is virtually based on the theorem that half the *mean* energy of an undulation is equal to the illumination produced.

18 The quantum theory, however, definitely asserts that the mean energy radiated is proportional to the frequency. On the undulatory theory also, the mean kinetic energy or illumination refers to a particular wave-length or frequency and is, so far, ascribed a discrete existence. But a nearer concordance may be reached by identifying the energy of radiation with that given by Larmor's expression, viz. $\frac{2}{3}\frac{e^2}{c}\int f'^2\,dt$, if we confine ourselves to a vibrating electron (*e.g.* a Bohr electron vibrating in the disturbed orbit of art. 10). Now if v = velocity (vibrational) of the Bohr electron (in the disturbed orbit), relative to the steady motion, $v = v_0 \sin pt$, say ; then

$$\frac{2}{3}\frac{e^2}{c}\int f^2\,dt = \frac{4}{3}\pi^2\frac{e^2}{c}v_0^2\nu.$$

[This makes v_0 an absolute constant, for $\frac{4}{3}\pi^2\frac{e^2}{c}v_0^2 = h$.]

19. It is, of course, easy to see that the equation (7) (art. 2) is really based on two postulates, (1) that the change of energy is impulsive, (2) that the impulsive change of energy or the time integral of energy is atomic.

20. With regard to the second principle (that the time integral of energy is atomic) it recalls the familiar equation $\int i\,dt = (n+n')e$, where i is the electric current and $\int i\,dt$ is the total charge on $n+n'$ ions.

This is, perhaps, more than an analogy, for it seems to be pretty evident, as Jeans has pointed out, that the atomicity of h is associated with the atomicity of e, which has really been accepted so far as a fact without any physical explanation.

21. With regard to the first, it obviously recalls the well-known equation in Elementary Dynamics, viz., $\int F\,dt$ = change of momentum produced.

Although this equation is always true, its use is practically confined in ordinary Dynamics to the case in which a large force (an impulsive force) acts for a very short time, and in which, therefore, it is not convenient to consider the force and time separately. In strictness, however, this is the more fundamental equation and is, as is well known, the basis of Newtonian Dynamics.

Remembering that h or $h/2\pi$ is of the same physical dimension as angular momentum, as has been pointed out by Jeans, the equation $\int E\,dt = Nh$ as the basis of quantum Dynamics seems to be exactly analogous to the fundamental equation of ordinary Dynamics.

22. In his report on quantum theory Jeans mentions Sommerfeld's theory of an element of action represented by $h/2\pi$ or $h/4$, which serves to explain X-rays, γ-rays, and the photo-electric effect. Without going into the exact form of this theory, it is easily seen that such a theory is *a priori* justified in as much as these phenomena owe their origin to impulses. The present formulation rather aims at calling attention to the fact that just as we are led to the conception of finite forces, from that of impulsive forces, similarly the principle of impulsive change of energy contemplated in the quantum theory and that of a continuous change of energy of classical Dynamics may not be necessarily contradictory, and that we are apparently led to the same mechanism of the propagation of energy on the quantum theory as in the undulatory theory.

XXXVIII. *A new Discussion of Bucherer's Experiment.*

By G. A. Schott, *F.R.S.**

1. U. Doi† has published an article recently in this Journal with the above title, in which he claims that Bucherer's‡ well-known experiment decides in favour of a mass-formula for the electron proposed by Doi himself and against the mass-formula of Lorentz—to give it its usual name after the writer who first proposed it. In the course of his article Doi writes (*l. c.* p. 446) : "Now, it may be too

* Communicated by the Author.

† U. Doi, Phil. Mag. ser. 6, xlix. p. 434 (1925).

‡ A. H. Bucherer, *Ann. der Phys.* F. 4, Bd. 28, p. 518 (1909).

far here to enter into any speculative inquiry as to what disturbing cause should have given rise to these discrepancies. And yet it may be noticed, all the same, that some systematic or other error must have anyhow been inherent to Bucherer's estimation of the effective field-intensities at work." Clearly the very definite criticism of Bucherer's work implied in this quotation requires an answer; so also does the claim that Doi's discussion disposes of the Lorentz mass-formula. If I am undertaking the task of replying, it is for two reasons. In the first place, I was privileged to spend a great portion of an eighteen months leave of absence during 1907–1908 at work in Bucherer's private room in the Physical Institute of Bonn University, thanks to his and Professor Kayser's kind hospitality, at the very time the experiments in question were in progress, and thus was able to discuss the experimental arrangements and difficulties fully with Professor Bucherer. Secondly, soon after my return from Bonn I completed the determination of the path of the Lorentz electron in a field of the type used by Bucherer in his apparatus *, but failed in the attempt to apply this method to the estimation of the effect on the film of the so-called non-compensated β rays, to which Bucherer and myself were agreed in attributing the discrepancy now discussed by Doi, because at that time practically nothing was known about the distribution and intensity of the lines in the magnetic spectrum of radium. Some years ago, thanks to the researches of Danysz and of Ellis, information on this subject had increased so much that a new attack on the problem seemed justified, and therefore one of my pupils, Mr. T. Lewis., B.Sc., worked out a detailed method, which enabled him to specify the point of impact on the photographic film of an electron, projected from the grain of radium fluoride at the centre of Bucherer's condenser with any prescribed velocity in any prescribed direction. Thanks to Bucherer's kindness Lewis was able to measure what was left of the original films during the summer vacation of 1923 at Bonn and to complete his numerical calculations by October, 1924, when his paper was sent to the Royal Society †.

In this article I shall begin with the discussion of Doi's discrepancy and of its cause—the presence of non-compensated β rays—and also of the reasons which led Bucherer to relinquish his original idea of using the complete curve for

* Schott, 'Electromagnetic Radiation,' p. 301 (1912).
† Lewis, Proc. Roy. Soc., A vol. 107. p. 544.

the test of the various mass-formulæ and to rely on the comparison of the maximum deflexions obtained in experiments with different field-intensities. Then I shall compare Doi's mass-formula with the results of all six of Bucherer's published experiments, supplemented for higher velocities by four experiments made by Neumann by Bucherer's method and remeasured and recalculated by Schäfer *. This comparison affords a rigorous test of the mass-formula for velocities ranging from 0·3 to 0·85 times the velocity of light.

2. *Doi's discrepancy and the compensated β rays.*—The principle and details of Bucherer's method are so well known that no space need be wasted in explaining them. All that need be said is that the usual simple theory, as given for instance by Doi himself, only deals with a single class of electrons, the so-called compensated β rays. These pursue straight paths inside the condenser, owing to the fact that the—let us say downward—electric deflexion just neutralizes the upward magnetic deflexion. If all these electrons were projected horizontally and so traversed the condenser parallel to the plates they would produce a trace on the film of width 0·025 cm., exactly equal to the distance between the plates; but some of them, projected upwards or downwards, pass through in an inclined direction, the extreme ones from the centre of one plate to the edge of the opposite one. In Bucherer's apparatus the radius of the film was nearly twice that of the plates of the condenser, so that the width of the trace due to the compensated β rays should be three times the distance between the plates, viz. 0·075 cm., which is in fact the approximate width of the actual trace near the point of maximum deflexion, *i. e.* at an angular distance of 90° from the direction of the magnetic force. The velocity of the electrons which produce the maximum deflexion is β_0 times the velocity of light, where $\beta_0 = X/cH = \sin\alpha_0$ in Doi's notation; but that of those electrons which produce parts of the compensated ray trace at a distance from the maximum is greater: *e. g.*, at the angular distance α the velocity is β times the velocity of light, where $\beta = \beta_0 \operatorname{cosec}\alpha$. The mass-formula has not been used so far, so that agreement subsists between the different formulæ up to this stage. Both lead to the result that β is unity when $\sin\alpha = \beta_0$, and $\alpha = \alpha_0$, or $\alpha = \pi - \alpha_0$, so that the trace reaches from $\alpha = \alpha_0$ beyond the maximum to $\alpha = \pi - \alpha_0$, *when we confine our attention to the compensated β rays.* In Bucherer's

* C. Schäfer, *Ann. der Phys.* F. 4, Bd. 49, p. 934 (1916).

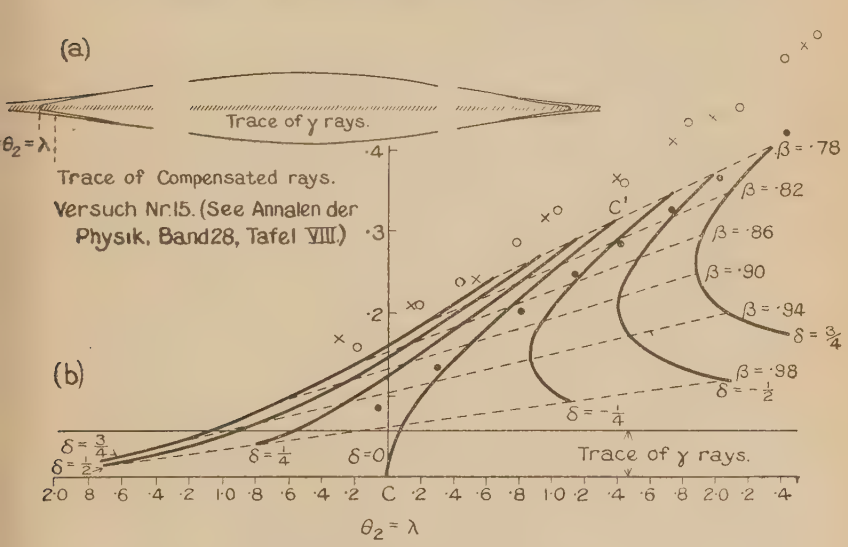
experiment no. 15, which has been discussed by both Doi and Lewis and is therefore specially suitable for our consideration, the value of β_0 is given by Bucherer as 0·5154, so that α_0 is almost exactly 31°. Thus the compensated β-ray trace should extend over 118° of the film, and its length should be nearly 16·5 cm., because the radius of the film was about 8 cm. The actual length of the trace is ill-defined, because the ends are much fogged, but it is about 19 cm. On p. 245 Doi calculates that this requires β_0 to be only 0·374, or 27 per cent. less than Bucherer's value, always on the supposition that the entire trace is due to compensated β rays alone and that the non-compensated β-rays are ineffective. Doi attributes this discrepancy to errors in the field-intensities, without giving any other reason for his conjecture. But anyone who knows the apparatus used and the precautions taken, cannot help being convinced that errors of this magnitude are utterly inconceivable. Hence we must look for some other cause for the discrepancy.

3. *The non-compensated β rays.*—These are constituted by electrons which pursue curved paths—approximately parabolas—inside the condenser, because the electric and magnetic deflexions, although in opposite directions, do not neutralize one another completely. Bucherer already in his first paper on p. 519 notes that these non-compensated β rays are mainly responsible for the ends of the actual trace and for the fogging in their neighbourhood; in § 5, p. 526, he discusses their role and on p. 527 writes: "In Übereinstimmung mit der Theorie erstreckt sich ihre Ablenkung z über eine grosse Strecke, so dass ein breites Band entsteht, welches bis zur γ-Linie reicht und nur auf der konvexen Seite ziemlich scharf begrenzt ist. Diese Erscheinung zeigen sämmtliche Aufnahmen in der Nähe des Schnittpunktes der Kurve mit der γ-Linie." Further on he discusses the effect of the non-compensated rays on the maximum deflexion and concludes that the consequent error in the value of e/m_0 cannot exceed one half of one per cent. In view of all this and of his constant reference to Bucherer's paper, it is difficult to understand why Doi omits all reference to the non-compensated rays and uses the ends of the actual trace in his test of the mass-formulæ, when measurements in that region are known to be unreliable.

4. In the paper already referred to Lewis has made a point of studying the non-compensated rays in detail (*l. c.* § 5 to 8) and has summarized the results of his calculations and measurements in a table on p. 560 and a diagram, fig. 3, of which the latter is reproduced here by the kind permission

of the Council of the Royal Society. This diagram gives a graphical representation of one of Bucherer's films in the immediate neighbourhood of one end of the actual trace, the value of β_0 being 0·5154. It is uncertain whether this particular film is the one actually taken in experiment no. 15, but at any rate it was taken under exactly the same conditions and gave the same maximum deflexion. The horizontal scale of the diagram, marked along the middle of the undeflected γ-ray line, is about 3·5 times the actual, whilst the vertical scale is 5 times greater still.

The curve CC′ is the middle line of the trace of the compensated β rays calculated according to the Lorentz



[Fig. 3, Proc. Roy. Soc. A, cvii.]

mass-formula, so that the point C is about 31° to the right of the intersection of the film with a diameter of the condenser parallel to the magnetic force, and 59° to the left of the maximum of the trace. The curve CC′ is very nearly parabolic with C as vertex, and accordingly cuts the γ-ray line perpendicularly, as Doi points out on p. 440.

Besides this curve Lewis shows six curves of a family defined by a certain parameter δ, of which family the curve CC′ is one, being defined by δ zero. These curves are drawn as full lines, to the left of CC′ for positive values of δ, to the right for negative values. They approach very close to the γ-ray line at one end and to the curve CC′ at

the other at large distances from C. Like the curve CC′ itself they are to be regarded as the middle lines of narrow strips or traces, due to pencils of non-compensated β rays; they themselves are produced by electrons passing through the condenser symmetrically along approximately parabolic paths with vertices or turning points halfway between the centre and edge. The parameter δ measures the distance of the vertex below the median plane of the condenser on such a scale that the values $\delta = \pm 1$ correspond to vertices on the plates themselves. The remainder of each strip or trace is due to electrons whose paths deviate slightly from the symmetrical paths, and the number of them falling on an element of the trace of given length diminishes as the numerical value of δ increases; for instance Lewis estimates that the intensity of the traces $\delta = \pm 0{\cdot}75$ is about three-quarters of that of the trace δ zero, whilst their width is about 0·95 as great. These strips may be regarded as filling the whole of the area of the film, but their effect is only appreciable along the trace of the compensated rays, except near its ends, where it extends considerably beyond, to each side, as we see from the diagram.

Besides the family δ Lewis has constructed a second family defined by the parameter β, which denotes the ratio of the velocity of projection of the electron from the radium grain to the velocity of light. The curve β unity coincides with the γ-ray line, whilst the others lie above it in order, rising successively more and more steeply from left to right.

In addition Lewis has represented the readings taken by him of points on the outside edge of the actual trace on film no. 15 near its ends by circles and crosses respectively, each representing the mean of five or six readings, usually differing by less than one tenth of one millimetre. The inner edge of the trace is too much fogged for accurate measurement, but its approximate position is marked by black dots.

The diagram shows that the curves $\delta = \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$, within the range from $\beta = 0{\cdot}78$ to $\beta = 0{\cdot}94$ or $0{\cdot}98$, fall inside the actual trace within a distance of from one to one and a half centimetres, *i. e.* an angular distance of from seven to ten degrees, from the point C, the theoretical end of the trace of the compensated β rays according to the Lorentz formula and Bucherer's values of the field-intensities. Thus there can be no doubt that the presence of such non-compensated β rays in sufficient numbers would be quite sufficient to account for the ends of the actual trace; moreover, such β rays have been observed by Danysz in the magnetic

spectrum of radium. Consequently Doi's criticism of the Lorentz mass-formula and of Bucherer's experiments becomes pointless; there is no sufficient reason for assuming the presence of large errors of field-intensities in Bucherer's measurements.

Lewis has shown two things: (1) the effect of non-compensated β rays in falsifying the theoretical trace near its ends, so that accurate measurements in that region become impossible, at any rate until we have much more information as to the distribution of intensity in the magnetic β-ray spectrum of radium; and (2) the substantial accuracy of measurements of the trace in the neighbourhood of the maximum deflexion, as already proved by Bucherer in § 5 of his paper. These two results on the one hand demonstrate the soundness of Bucherer's procedure in confining his calculations to the maximum and on the other hand indicate the danger underlying Doi's method of utilizing the whole of Bucherer's curve, just as if each part of it were equally reliable. It is I think quite clear that it is unjustifiable to neglect the effect of the non-compensated β rays at a distance from the maximum.

5. *Doi's Table II.*—Doi lays great stress on the better agreement, as he maintains, with Bucherer's actual curves of those calculated by his own formula as compared with those calculated by the Lorentz formula. Quite apart from the danger already indicated of using the whole of one of Bucherer's for such a comparison, it will be worth while to examine Doi's claim more closely, especially regarding his Table II., because this table deals with Bucherer's curve no. 15, which was considered in detail by Lewis. It seems to me that the arrangement of Doi's tables may lead to a false impression, for my recalculations of some of his figures selected at random indicate that the terms in the same row of the columns headed α, β, z_E and z_D appear to belong together, as do those of columns x and $z_{\text{photogr.}}$, but the two sets of columns do not correspond. For instance, since the radius of the film was 8 cm., as assumed by Doi himself, the value $\alpha = 31°$ corresponds to $x = 8(\pi/2 - \alpha) = 82{\cdot}4$ mm., and not to $x = 95$ mm., which is the value placed by Doi in the same row. In other words, Doi apparently does not compare the calculated and observed deflexions for the same ordinate of the film, which seems to me to be the correct procedure. I have followed this procedure in rearranging Doi's Table II., calculating the values of $z_{\text{photogr.}}$ by interpolating between the numbers given by Doi. The result is shown in Table I. below for some of the values of α used by Doi, and is

somewhat surprising in so far as the Lorentz formula with this arrangement actually agrees better with Doi's measurements of Bucherer's curve than does Doi's own formula. My recalculations tend to show that Doi's values for both z_E and z_D are a little too low, so that the agreement of the Lorentz mass-formula with Bucherer's curve is quite good from the maximum at $\alpha = 90°$ down to $\alpha = 60°$, that is, for the middle half of the trace.

TABLE I. (Doi's Table II. rearranged.)

α degrees	90.	80.	70.	60.	50.	40.	35.	31.
x mm.	0	13·96	27·92	41·89	55·85	69·81	76·79	82·38
z_E mm.	10·35	9·93	8·75	7·03	4·98	2·80	1·65	0
z_D mm.	10·35	9·87	8·52	6·56	4·28	1·96	0·84	0
$z_{photogr.}$ mm. ...	10·3	9·98	8·93	7·30	5·48	3·53	2·57	1·72

Of course this rearrangement means giving up the attempt to make the end of the theoretical trace at $\alpha = 31°$ fit the end of the actual trace at about 22°, but it seems to me to be more in accordance with the experimental fact of the fogging of the plates near the end of the trace and its probable explanation by means of the non-compensated rays. At any rate the result that the role of the two mass-formulæ can be interchanged by a mere rearrangement of Doi's table, so as to favour the Lorentz formula instead of that of Doi, proves that there is an arbitrary element in Doi's method of comparison. In view of the uncertainty, which unavoidably attaches to the interpretation of Bucherer's curves near their ends, the only sound method is that used by Bucherer himself and his successors, viz. to compare the maximum deflexions obtained with different field-intensities. I shall now apply this method to Doi's formula.

6. *Comparison of Doi's mass-formula with the results of Bucherer and Schäfer.*—For convenience' sake I shall use Doi's notation, but shall distinguish between the two mass-formulæ by using plain letters for that of Lorentz and accented letters for that of Doi. Thus, for example, X and H will denote the electric and magnetic field-intensities as measured by Bucherer and Neumann and used with the Lorentz formula, whilst X′ and H′ will denote the values that must be attributed to them in order to bring Doi's formula into harmony with the experimental results according to his method of calculation. Let us begin by discussing

Doi's results for Bucherer's experiments nos. 7 and 15, given by him at the foot of his Tables I. and II. on pages 438 and 439.

Doi's expressions on page 436 give for the mass-formula of

$$\text{Lorentz}: e/m = (e/m_0)\cos\alpha_0, \quad . \quad . \quad . \quad . \quad (1)$$
$$\text{Doi} \quad : e/m = (e_0/m_0)\cos^2\alpha_0'. \quad . \quad . \quad . \quad (2)$$

The factors e/m_0 and e_0/m_0 both represent the specific charge of the resting electron, the value assumed by Doi on p. 446 being $1{\cdot}769 \,.\, 10^7$ e.m.u.

Doi's equations (5) and (6) give, with $\sin\alpha_0 = X/cH$, $\sin\alpha_0' = X'/cH'$,

$$e/m_0 = X/H^2C_E = (c/rH)\tan\alpha_0, \quad . \quad . \quad . \quad . \quad . \quad (3)$$
$$e_0/m_0 = X'/H'^2C_D = (c/rH')\sin\alpha_0'\sec^2\alpha_0'. \quad . \quad . \quad (4)$$

These equations hold for the maximum deflexion, given by $\alpha = 90°$, r denoting the radius of curvature of the path of the compensated β ray which produces this part of the trace. Being calculated from the maximum deflexion z and the constants of the apparatus, r is the same for both formulæ, but varies from one experiment to another. Since e/m_0 and e_0/m_0 are also the same, we obtain by comparing (3) and (4)

$$H'\cot\alpha_0'\cos\alpha_0' = H\cot\alpha_0. \quad . \quad . \quad . \quad . \quad (5)$$

We also have $(H'/X')\sin\alpha_0' = (H/X)\sin\alpha_0$; hence

$$X'\cot^2\alpha_0' = X\cot\alpha_0\,\mathrm{cosec}\,\alpha_0. \quad . \quad . \quad . \quad . \quad (6)$$

7. If all Bucherer's and Neumann's curves existed in their entirety, we could determine α_0' directly from the measured length of the trace, it is true only with a large error, but quite accurately enough for our purpose. Unfortunately most of Bucherer's films are lost, whilst Neumann only used the part near the maximum, so that only two complete curves are available, viz. those used by Doi, nos. 7 and 15. Doi finds for experiment no.

$$7: \alpha_0' = 19°{\cdot}1 \text{ instead of } \alpha_0 = 25°{\cdot}35,$$
$$15: \alpha_0' = 22°{\cdot}0 \text{ instead of } \alpha_0 = 31°{\cdot}03.$$

From (5) and (7) we obtain for experiment no.

$$7: H/H' = 1{\cdot}29,\ X/X' = 1{\cdot}69,$$
$$15: H/H' = 1{\cdot}38,\ X/X' = 1{\cdot}90.$$

In other words, in order to bring Doi's formula into approximate agreement with the measured lengths of the traces it is necessary to suppose that Bucherer overestimated his magnetic field-intensities by amounts varying from thirty

to forty per cent., and his electric field-intensities by amounts varying from seventy to ninety per cent. Not only are these supposed errors impossibly large, but they must vary from one experiment to another, not in a haphazard, but in a perfectly definite manner. Although it must be admitted that the vacuum pumps available at the time of the experiments were much inferior to those in use now, yet the precautions taken by Bucherer to keep his vacuum low and to test it continually were sufficient to exclude large errors in the determination of the electric field-intensity. As regards the magnetic field-intensity the conditions were still more favourable, so that the error could hardly exceed one fifth of one per cent., for the magnetic field was produced by a standardized coil without any iron in its neighbourhood, the currents being kept constant and measured by means of a standardized Siemens precision ammeter.

8. We can however apply a more complete test, and one perhaps more favourable to Doi's formula, if we compromise by assuming that the magnetic field-intensity was measured accurately, so that $H' = H$. Then (5) gives

$$\cot \alpha_0' \cos \alpha_0' = \cot \alpha_0. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This equation determines α_0' from α_0 and enables us to dispense with the necessarily inaccurate measurement of the length of the trace. We can now calculate l', the length of the trace needed on the present supposition by Doi's formula, and also l, that needed by the formula of Lorentz, and compare them with the measured length, at least for the two films available. We can calculate the electric field-intensities X′ and X as before. This procedure amounts to distributing the error between the measurements of the length of the trace and of the electric field-intensity (ur). In this way I have calculated the following table for the five values of β_0 used by Bucherer (the first five rows of the table) and the two values used by Schäfer (the last two rows).

TABLE II.

β_0.	α_0.	α_0'.	β_0'.	l.	l'.	X/X′.	l/l'.	l obs.
0·3173	18° 30′	17° 41′	0·3037	20·0 cm.	20·2 cm.	1·045	0·990	—
3787	22 15	20 53	3570	19·0	19·3	1·061	984	—
4281	25 21	23 29	3985	18·1	18·6	1·074	973	19·8 cm.
5154	31 1	27 58	4690	16·5	17·3	1·099	952	19·0
6870	43 24	37 3	6025	13·0	14·8	1·140	878	—
80	53 5	43 50	69	10·3	12·9	1·16	80	—
85	58 13	47 29	74	8·9	11·9	1·15	75	—

The last column gives the lengths of the actual traces measured by Doi on films nos. 7 and 15.

This table shows us three things: (1) the error in the electric force needed to bring Doi's formula into harmony with the results of Bucherer and of Neumann, as recalculated by Schäfer, increases to a maximum of about sixteen per cent. as the corrected velocity β_0' increases to the value 0·7; (2) the length of the trace l', calculated from Doi's formula, exceeds l, that calculated from the Lorentz formula, by an amount which increases relatively and absolutely as β_0' increases; (3) the value of l' is still much below the measured value, to judge from Bucherer's experiments nos. 7 and 15, so that the discrepancy pointed out by Doi still exists, though in a slightly mitigated form.

Thus, even if we could admit the possibility of imperfections in the value of Bucherer's and Neumann's experiments just sufficient to account for the hypothetical errors in the electric field-intensities and of just the right amount to explain the very particular law of dependence of the errors on the velocities used, we should not thereby dispose of Doi's discrepancy and should still be compelled to invoke the help of non-compensated β rays to account for the unexplained balance. The Lorentz formula on the other hand needs no such errors in the field intensities; it only requires us to take into account the presence of non-compensated β rays in order to explain the deviations near the ends of the traces, where we know already that measurements are exceedingly unreliable. In view of these facts there does not seem to me to be any sufficient reason for rejecting the Lorentz mass-formula in favour of that of Doi, at any rate for values of β less than 0·8 or 0·85. Nevertheless experiments with improved apparatus are very much to be desired, in order to test the formula in the neighbourhood of and beyond this limit.

XXXIX. *The Two-Stage Transformation of Magnetite into Hematite.* *By* Lars A. Welo *and* Oskar Baudisch *.

(From the laboratories of the Rockefeller Institute for Medical Research, New York.)

WE have been engaged during the past year in the study of a certain chemical reaction † in which one of the final products is a magnetic oxide of iron. It is a ferro-ferric oxide of the composition $2FeO, 3Fe_2O_3$. It was

* Communicated by the Authors.

† O. Baudisch and P. Mayer, *Biochem. Z.* cvii. p. 1 (1920); and O. Baudisch and L. A. Welo, J. Biol. Chem lxvi. p. 261 (1924).

natural to compare its properties, both physical and chemical, with those of the more common ferro-ferric oxide FeO, Fe_2O_3, which is magnetite and usually written Fe_3O_4. At the same time a comparison was made with the oxide of Haber and Kaufmann*, which also has the composition $2FeO, 3Fe_2O_3$, but is made in a different manner. During this work of comparison it was discovered that the process of transformation of each of these ferro-ferric oxides into the non-magnetic ferric oxide Fe_2O_3 takes place in distinct stages, and that the disappearance of the magnetism by heating is dependent on the existence of a preliminary oxidation.

Our work on the intercomparison of the properties of the three oxides is about complete, and a full report on it is to be published. In the present paper we shall be concerned only with the conditions which govern the transformation of each of these magnetic ferro-ferric oxides into the non-magnetic ferric oxides. The conditions are the same for each of them; at least they are qualitatively so. It will be sufficient, for the purpose of this paper, to describe the steps of the transformation of the magnetite, FeO, Fe_2O_3, into the non-magnetic, purely ferric oxide, Fe_2O_3.

Preparation of Magnetite.

The magnetite used in this study was the black, microcrystalline substance formed when a solution containing one mol of ferrous sulphate and two mols of ferric sulphate is poured into a boiling solution of sodium hydroxide. It is necessary that sodium hydroxide be present in excess so as to give, always, an alkaline solution. The precipitate was washed until the filtrate showed no alkali when tested with litmus paper. After collection on a filter the oxide was dried in a desiccator.

The Qualitative Observations.

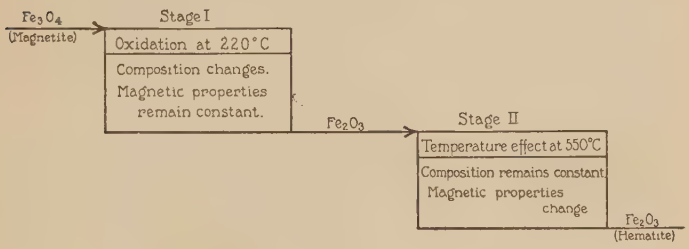
Generally speaking, the facts observed on heating the oxide in a stream of oxygen are as follows:—The colour of the oxide changes suddenly from black to a dark red at about 220° C.; the oxide remains magnetic, although the iron has been completely converted into the ferric form so that the composition has become Fe_2O_3. The ferricyanide test showed not a trace of Prussian blue, and hence no

* F. Haber and A. Kaufmann, *Z. Elektrochem.* vii. p. 733 (1900–1901).

ferrous iron after oxidation for a sufficient time at 220° C. A solution of the oxide in hydrochloric acid titrated with potassium permanganate likewise yielded no iron in the divalent form. All of this shows that Fe_3O_4 may be completely oxidized to Fe_2O_3 at a temperature of 220° C. without loss of the magnetic properties.

On further heating, the oxide, now Fe_2O_3, remains magnetic until a temperature of 550° C. is reached. At this temperature a non-reversible transformation takes place, for the oxide becomes permanently non-magnetic. This transformation is obviously a pure temperature effect, since the oxidation was already complete at the lower temperature of 220° C. But to test the point a sample which had first been oxidized at 220° C. was heated in an atmosphere of nitrogen carefully freed from oxygen. It again became non-magnetic. The necessary condition, however, for the loss of magnetism at 550° C. is that the Fe_3O_4 must first be oxidized to Fe_2O_3 at some lower temperature. If Fe_3O_4 is

Fig. 1.



heated in nitrogen without a preliminary oxidation it is stable, and retains its magnetic properties even if heated to 800° C. These observations are briefly summarized in the scheme shown in fig. 1.

It has been stated that the oxidation begins at 220° C. A more precise statement would be that the oxidation becomes sufficiently rapid at that temperature so that the change in colour may be observed. It is recognized that oxidation may take place at a much lower temperature.

It is interesting to note here that the temperature of stage II. is found to be nearly the same as, and probably does actually coincide with, the Curie point for natural magnetite, which is 525° C., according to Graetz *.

* Graetz, 'Handbuch der Elektrizität und des Magnetismus,' vol. iv. p. 888.

The Permeabilities.

It was decided to make more precise measurements of the permeabilities on the original Fe_3O_4 and on the derived oxides after each stage of the transformation. A long magnetizing solenoid of two layers was wound on a brass tube. There were 13·6 turns per centimetre, so that the field intensity turns out to be 17·1 gauss per ampere. Another brass tube was made to fit into the tube carrying the solenoid. On this second brass tube circular grooves were cut to make room for test coils of, respectively, 4, 20, and 100 turns. The leads were carried to binding-posts at one end so that any one of the coils could be connected to a high sensitivity Leeds & Northrup ballistic galvanometer. The oxides were packed by jarring (not by tamping) into a glass tube which slipped into the second brass tube. The length of packing was always 20 centimetres, so the demagnetizing factor becomes entirely negligible. The densities of packing could not be regulated, but were never far from an average value of 1·32 $\frac{\text{gr.}}{\text{cm.}^3}$. The corrected permeabilities μ_c were calculated from the observed permeabilities μ_o by the relation

$$\mu_c = (\mu_o - 1)\frac{1{\cdot}32}{\delta_p} + 1,$$

where δ_p is the density of packing.

The fact that these oxides have permeabilities of about 3 at the most simplifies the procedure. The galvanometer deflexions with oxide in the glass tube and with the tube empty are of the same order of magnitude, and their ratio R, for a given magnetizing field, can be introduced directly into the formulæ.

Let A_o be the internal cross-section of the glass tube containing the oxide, and A_e be the mean area of the test-coil wound on the brass tube.

With the empty tube the flux through the coil is A_eH and the deflexion

$$d_e = CA_eH,$$

C being a constant.

With oxide in the tube the flux is

$$(A_e - A_o)H + A_oB = (A_e - A_o)H + A_o\mu H,$$

so that the deflexion

$$d_o = C[(A_e - A_o)H - A_o\mu H],$$

$$\frac{d_o}{d_e} = \frac{(A_e - A_o)H + A_o\mu H}{A_eH} = R,$$

giving

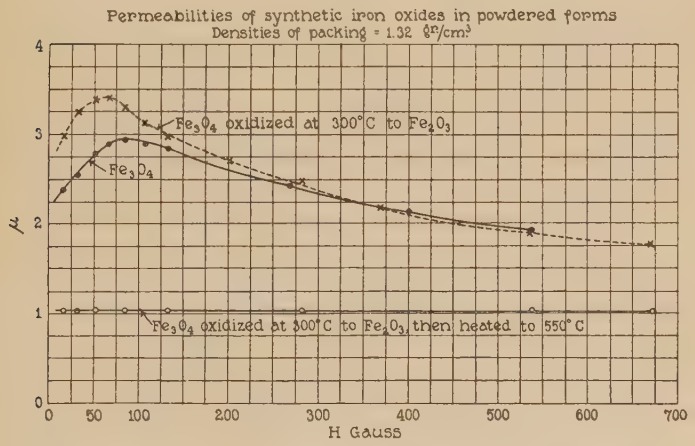
$$\mu = \frac{A_o}{A_e} R - \frac{A_e - A_o}{A_o},$$

and, if we desire, an equally simple derivation of the induction

$$B = \frac{H}{A_o}[RA_e - (A_e - A_o)].$$

Field intensities greater than 85 gauss could not be obtained without undue heating of the solenoid, so that another was used for the stronger fields. It carried several hundred turns. As it was rather irregularly wound it had to be calibrated, and was found to give a field intensity of 134·2 gauss per ampere.

Fig. 2.



The results of the magnetic measurements are shown in fig. 2. Our qualitative observations are confirmed. The maximum permeability of the oxide after having passed the first stage of transformation is somewhat higher than that of the original Fe_3O_4, and there is shown a considerable shift of its position. No reason is known for this. At higher fields the curves coincide, which accounts for our qualitative observation (made with high field intensities) that the magnetic properties remain unchanged on oxidation at a low temperature. After the second stage the permeability is seen to be nearly, but not quite, unity at all fields. The maximum residual permeability is 1·045, and is so small that the material would be considered non-magnetic towards rough qualitative tests.

The Change in Structure.

The crystal structures of magnetite and hematite are known to be different. Bragg * and Nishikawa † found for magnetite a diamond-point structure, and Davey ‡ found that hematite is like corundum, which, in turn, resembles calcite. It was of interest to determine whether the change of one structure into the other takes place at stage I. or at stage II. It seemed improbable that it changes at stage I. on account of the constancy of the magnetic properties when the oxide passes through that stage. On the other hand, it was difficult to assume that it changes on stage II., for it would involve the assumption that Fe_2O_3 has allotropic forms, and can assume either the form found for magnetite or the calcite structure usually obtained for hematite.

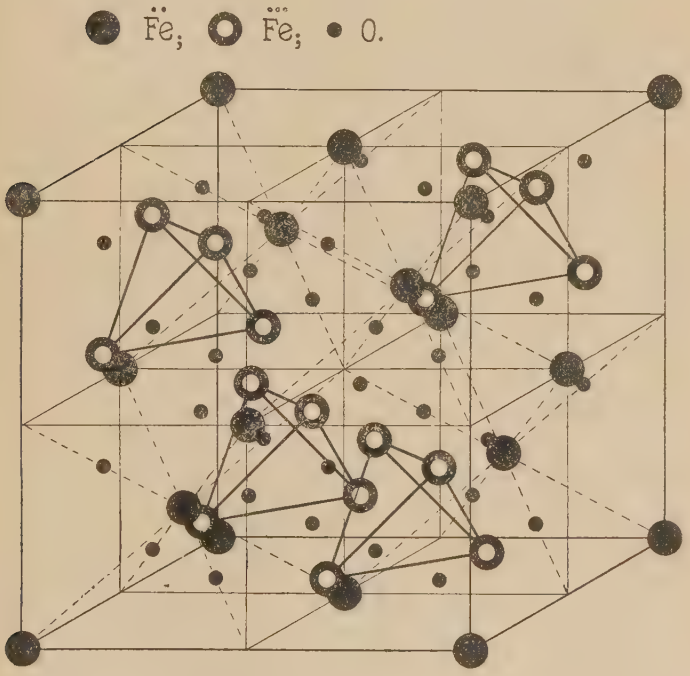
Diffraction patterns of the original Fe_3O_4 and the resulting oxides after each stage of transformation were obtained for us by Dr. Wheeler P. Davey, of the General Electric Company, to whom we herewith express our thanks. The original Fe_3O_4 and the Fe_2O_3 which had passed through stage I. gave identical patterns, and the spacings were the same to within one-tenth of one per cent. The Fe_2O_3 which had been through stage II. of the transformation, however, showed the pattern usually found for Fe_2O_3. The disappearance of the magnetic properties of the oxide is therefore associated with the change in structure taking place at stage II., and is not connected with the change in composition. It is also evident that the atoms of iron and oxygen in Fe_2O_3 have two alternative arrangements in the crystal. If Fe_2O_3 is derived by oxidation of Fe_3O_4 at a low temperature, the Fe_3O_4 structure is retained, and only at a higher temperature of about 550° C. does this structure become unstable and change into the more stable one similar to calcite. The original Fe_3O_4, however, as has already been pointed out, remains stable up to temperatures of at least 800° C. if we prevent oxidation to Fe_2O_3.

This result suggested the interesting problem of finding room for more oxygen in a crystal of Fe_3O_4 without a change in the arrangement of the atoms already in place. We are indebted to Dr. L. W. McKeehan and Dr. R. M. Bozorth, of the Western Electric Company, for aid in this part of the study.

* Bragg, Phil. Mag. xxx. p. 305 (1915).
† Nishikawa, Proc. Math. Phys. Soc. Tokyo, viii. p. 199 (1915).
‡ Davey, Phys. Rev. xxi. (6) p. 716 (1923).

Fig. 3 shows the unit cube for magnetite as constructed from data given by Wyckoff *. The unit cube contains eight molecules, so that Fe_3O_4 may be written $Fe_{24}O_{32}$. After oxidation to Fe_2O_3 the corresponding composition would be $Fe_{24}O_{36}$. We must find room for four additional oxygen atoms in the cube. The first places to suggest themselves are the centres of the tetrahedra formed by the

Fig. 3.



MAGNETITE

trivalent iron atoms, and they are thus shown in fig. 4. In view of the uncertainties as to the actual radii of combination, it is quite possible for the extra oxygen atoms to be placed, as shown, without undue distortion of the system. The edge of the unit cube has a length $a = 8{\cdot}30$ Å., and the distance from the centre of the tetrahedron formed by trivalent iron atoms to each corner is

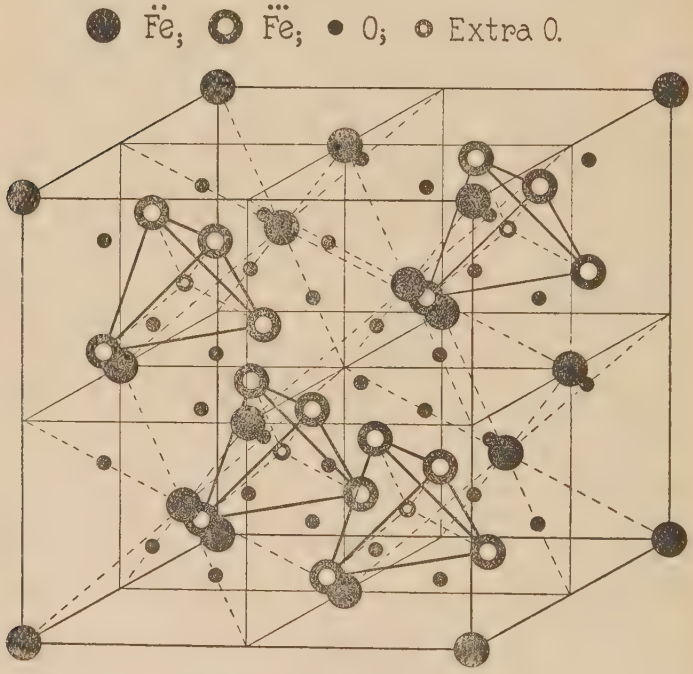
$$\frac{a}{8}\sqrt{3} = 1{\cdot}795 \text{ Å}.$$

* Wyckoff, Journ. Franklin Inst. cxcv. pp. 531, 544 (1923).

The radius of the oxygen atom is usually taken to be 0·65 Å. This leaves 1·145 Å. as a remainder for the radius of the iron atom. The radius of the iron atom appears to be variable, and values as low as 1·25 Å. have been found in the case of pyrites * and in iron itself.

An alternative and perhaps equivalent arrangement would be to place an oxygen atom at the middle of each edge of the unit cube. The room at our disposal would be the same. This question is not considered here, as it would

Fig. 4.



OXIDIZED MAGNETITE

require a more detailed study of the diffraction pattern, and would probably be indeterminate even then. We are here concerned only with the possibility of putting more oxygen in magnetite so as to change it to hematite without changing the existing arrangement of the atoms.

A few remarks may appropriately be added here regarding an earlier objection to our interpretation which has now no force, since we see that it is possible to convert Fe_3O_4 to

* 'X-Rays and Crystal Structure,' W. H. and W. L. Bragg, 4th Edition, p. 172.

Fe_2O_3 without disturbing the structure. The contention was made that on the first stage the oxidation was only superficial, and that the cores of the particles remained unchanged. It was supposed that complete oxidation took place only at the higher temperature. The superficial layer of Fe_2O_3 formed, then, on stage I. would form so small a proportion of the whole that the magnetic properties and the diffraction pattern would appear unchanged. The fact that the oxide which has been through stage I. loses its magnetism and changes its structure when heated in nitrogen to 550° C. makes this improbable. The improbability is heightened by the fact that unoxidized Fe_3O_4 remains magnetic after heating in nitrogen to a still higher temperature. The nitrogen cannot contain sufficient oxygen as an impurity to bring about the necessary oxidation. That the oxidation is not superficial is shown also by the chemical tests for ferrous iron, for in these tests the whole particle, core and surface, is first dissolved in hydrochloric acid. To make doubly sure, a test was made for increase in weight when the transformation at stage II. takes place in a stream of oxygen. Instead of the calculated increase of 32 milligrams, for the particular sample used, there was a decrease in weight of about one milligram.

The Order of the Oxidation Process.

We are now in possession of an unforced explanation as to why the presence or absence of magnetism in the synthetic ferric oxide Fe_2O_3 depends on the order in which the chemical operations are carried out. Hilpert * oxidized an existing ferro-ferric oxide into the ferric oxide by means of the strong oxidizing agents H_2O_2 and $K_2S_2O_8$, and found the product to be magnetic. On the other hand, we † have precipitated ferrous hydroxide in the presence of the same oxidizing agents, and the resulting oxide Fe_2O_3 is non-magnetic. The two cases may be represented by

$$(1)\ FeSO_4 + 2NaOH + xO_2 \rightarrow xFe_3O_4 + x\left[\begin{matrix} H_2O_2 \\ \text{or} \\ K_2S_2O_8 \end{matrix}\right] \rightarrow xFe_2O_3 \quad \text{Magnetic.}$$

$$(2)\ FeSO_4 + 2NaOH + x\left\{\begin{matrix} H_2O_2 \\ \text{or} \\ K_2S_2O_8 \end{matrix}\right\} \rightarrow xFe_2O_3 \quad \text{Non-magnetic.}$$

In case (1) the oxide first formed is magnetite, and it retains its structure in spite of the subsequent oxidation to Fe_2O_3. In case (2) the conditions of precipitation are such that the usual Fe_2O_3 structure is built up from the start.

* Hilpert, *Ber. Chem. Ges.* xlii. p. 2248 (1909).

† O. Baudisch and L. A. Welo, Journ. Biol. Chem. lxi. p. 261 (1924).

Summary.

It is shown that the ferro-ferric oxide Fe_3O_4 (magnetite) can be completely oxidized to Fe_2O_3 at a low temperature of 220° C., so that the maximum permeability may even rise from 2·93 to 3·39, the density of packing of the powders being 1·32 gr./cm.^{3} Then, if this ferric oxide is heated in a neutral atmosphere of, say, nitrogen at about 550° C., the maximum permeability falls to 1·045. The nearly total loss of permeability is therefore purely a temperature effect. But the necessary condition is that the ferrous iron in Fe_3O_4 must first be oxidized to the ferric form. If Fe_3O_4 is not first oxidized, it may be heated in the absence of oxygen to at least 800° C. without permanent loss of permeability.

The change in crystal structure came on the second stage; that is, the oxide Fe_2O_3 had the same structure as the original Fe_3O_4, and did not assume the structure usually found for Fe_2O_3 until the temperature of 550° C. had been reached. An oxide of the composition Fe_2O_3 can therefore have two structures. It is shown that there is room for more oxygen in the atomic arrangement of magnetite without undue strain on the structure. It is pointed out that the results account for the formation of magnetic or non-magnetic ferric oxides according to the order of the chemical operations.

February 20, 1925.

Note added on reading proof.

Our attention has been called to an article by Sosman (Journ. Wash. Acad. Sci. vii. p. 65, 1917), in which he discusses the properties of magnetic ferric oxide, and refers to earlier studies. These studies include that of Hilpert, with which we were already familiar, as shown by our reference. None of these papers, however, bring out the fact that the change in the crystal structure of the oxide and the change from the magnetic to the non-magnetic form take place together.

Since our paper was written we have attempted similar work with natural magnetite. It appears that the transformation at stage I. can be carried out but only at a much higher temperature (about 800° C.). The transformation at stage II. cannot be carried out at any temperature below that at which the Fe_2O_3 begins to decompose. (See Sosman and Hostetter, Bull. Amer. Inst. Min. Eng. cxxvi. p. 930, 1917.)

XL. *An Extension of the Theorem of the Virial.* By Prof. E. A. Milne *.

THE equations of motion of a particle of mass m at a point (x, y, z) moving under a force whose components are X, Y, Z, are

$$m\ddot{x} = \mathrm{X}$$

and two similar equations. Using the identity

$$\frac{1}{2}\frac{d^2}{dt^2}(x^2) = \dot{x}^2 + x\ddot{x},$$

we have

$$\tfrac{1}{4}m\frac{d^2}{dt^2}(x^2) - \tfrac{1}{2}m\dot{x}^2 = \tfrac{1}{2}\mathrm{X}x.$$

Adding together this and two similar equations and summing for a number of particles, we find

$$\frac{1}{4}\frac{d^2}{dt^2}(\Sigma mr^2) = \tfrac{1}{2}\Sigma mv^2 + \tfrac{1}{2}\Sigma(\mathrm{X}x + \mathrm{Y}y + \mathrm{Z}z),$$

where

$$r^2 = x^2 + y^2 + z^2, \quad v^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2.$$

Integrate through a period of time τ, and use bars to denote mean values with respect to the time. Then

$$\frac{1}{4\tau}\left[\frac{d}{dt}(\Sigma mr^2)\right]_0^\tau = \tfrac{1}{2}\Sigma\overline{mv^2} + \tfrac{1}{2}\Sigma(\overline{\mathrm{X}x + \mathrm{Y}y + \mathrm{Z}z}).$$

If the motion of the system of particles is periodic and τ is a multiple of the period, the left-hand side vanishes. Again, if the system is statistically in a steady state the left-hand side can be made as small as we please by taking τ sufficiently large. In either case we have

$$\Sigma\overline{\tfrac{1}{2}mv^2} = -\tfrac{1}{2}\Sigma(\overline{\mathrm{X}x + \mathrm{Y}y + \mathrm{Z}z}). \quad . \quad . \quad . \quad . \quad (1)$$

The expression on the right-hand side of (1) was called by Clausius the virial, and the result expressed by (1) under the conditions stated is Clausius's famous Theorem of the Virial, first published by him in English in the Philosophical Magazine †.

It is the purpose of this note to point out that the Theorem of the Virial remains true of the particles are acted on by frictional forces proportional to their velocities in addition

* Communicated by the Author.

† "On a Mechanical Theorem applicable to Heat," Phil. Mag. ser. 4, xl. p. 123 (1870).

to the forces X, Y, Z. In other words, frictional forces proportional to velocities can be omitted in computing the virial. The proof is simple.

If the particle of mass m is acted on by a frictional force of magnitude kv, the equations of motion are of the type

$$m\ddot{x} = \mathrm{X} - k\dot{x}.$$

When this is multiplied by $\frac{1}{2}x$, it may be written in the form

$$\frac{1}{4}\frac{d^2}{dt^2}(mx^2) + \frac{1}{4}\frac{d}{dt}(kx^2) - \tfrac{1}{2}m\dot{x}^2 = \tfrac{1}{2}\mathrm{X}x.$$

Hence, adding three similar equations,

$$\frac{1}{4}\frac{d^2}{dt^2}(\Sigma mv^2) + \frac{1}{4}\frac{d}{dt}(\Sigma kv^2) = \tfrac{1}{2}\Sigma mv^2 + \tfrac{1}{2}\Sigma(\mathrm{X}x + \mathrm{Y}y + \mathrm{Z}z). \quad . \quad . \quad . \quad (2)$$

On integrating with respect to t as before, we notice that the terms arising from the frictions vanish if the state is steady, or if the motion is periodic and τ is a multiple of the period. Consequently (1) remains true as before. Frictional forces make no explicit appearance in the equation of the virial.

It may be noted that the presence of the frictional forces may alter the state of the system, and so alter the values of $\frac{1}{2}\Sigma\overline{mv^2}$ and of $-\frac{1}{2}\Sigma(\overline{\mathrm{X}x + \mathrm{Y}y + \mathrm{Z}z})$. But the two remain equal.

In many cases the presence of frictional forces forbids the existence of a steady state, so that the extension of the theorem is of limited application. Its utility will be sufficiently illustrated by the four following examples :—

I. *Forced vibrations.*

The first example is from elementary dynamics, and illustrates the case when the motion is periodic. Consider a particle moving in a straight line under the action of a controlling force $-mn^2x$, a friction $-k\dot{x}$, and an applied force $\mathrm{F}\cos pt$. The equation of motion is

$$m\ddot{x} + k\dot{x} = \mathrm{F}\cos pt - mn^2x.$$

Whatever the initial circumstances, the motion is known to be ultimately simple harmonic with period $2\pi/p$. Applying the extended theorem of the virial, we have

$$\tfrac{1}{2}\overline{m\dot{x}^2} = -\tfrac{1}{2}\overline{x(\mathrm{F}\cos pt - mn^2x)},$$

the means implying mean values through a period. If V denotes the potential energy of the particle in the field

of the controlling force, T the kinetic energy, this may be written

$$\overline{T}-\overline{V} = -\tfrac{1}{2}F\overline{x\cos pt}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which is the expression of the theorem of the virial for forced vibrations. It follows immediately that the average kinetic energy is less than or greater than the average potential energy according as the lag of phase of the particle behind that of the applied force is less than or greater than $\pi/2$. When the phase-difference is $\pi/2$, $\overline{x\cos pt}=0$ and $T=V$.

It is worth noticing that, once it is known that the motion is simple harmonic of period $2\pi/p$, the equation of the virial combined with the equation of the dissipation of energy determines the amplitude and phase of the vibration. From the equation of motion, on multiplying by $\dot{x}$ and integrating through a period, we have

$$(2k/m)\overline{T} = F\overline{\dot{x}\cos pt}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the well-known equation connecting the average kinetic energy with the mean rate of absorption of energy.

The amplitude and phase follow from (3) and (4) on substituting $x = x_0\cos(pt-\alpha)$ and evaluating the mean values.

II. *Motion of a star-cluster in a resisting medium.*

For a group of particles acted on only by their gravitational attractions, the virial is equal to minus one-half the gravitational potential energy. Let us denote the latter by $-\Omega$ $(\Omega>0)$. As was pointed out by Poincaré * and Eddington †, the theorem of the virial shows that, for a star-cluster in a steady state,

$$T = \tfrac{1}{2}\Omega.$$

When frictional resistances are acting on a group of gravitating bodies, as probably happened during the early history of the solar system ‡, there can be no steady state, but we can extend the above result in the form of an inequality. From (2) we have

$$T-\tfrac{1}{2}\Omega = \frac{1}{4}\frac{d^2}{dt^2}(\Sigma mr^2)+\frac{1}{4}\frac{d}{dt}(\Sigma kr^2).$$

* 'Hypothèses cosmogoniques,' p. 94 (1913).

† Monthly Notices R. A. S. lxxvi. p. 525 (1916). Also Jeans, 'Problems of Cosmogony,' p. 188 (1919).

‡ Jeffreys, 'The Earth,' chap. iv. (1924).

When Σmr^2 is a linear function of the time, the first term on the right-hand side vanishes. Now, when the rate of evolution (*i. e.* of contraction) is slow, we may adopt a linear approximation for Σmr^2 without serious error. The second term is essentially negative. We have then

$$T < \tfrac{1}{2}\Omega.$$

If W is the total energy of the cluster,

$$W = T - \Omega,$$

and the inequality may be written in either of the forms:

$$T < -W, \qquad -\Omega > 2W.$$

Thus the kinetic energy is less than minus the total energy; the potential energy exceeds twice the total energy. (*Cf.* Eddington, *loc. cit.*) Further, from the equation of the dissipation of energy,

$$\frac{d}{dt}(T-\Omega) = -\Sigma k^2,$$

we deduce, on eliminating Ω,

$$\frac{dT}{dt} = \frac{1}{2}\frac{d^3}{dt^3}(\Sigma mr^2) + \frac{1}{2}\frac{d^2}{dt^2}(\Sigma kr^2) + \Sigma k\dot{r}^2.$$

The first two terms will be small for slow evolution. Hence $dT/dt > 0$. It follows that the gain of kinetic energy due to contraction exceeds the loss due to friction.

III. *Brownian motion.*

The theory of the Brownian motion, in a liquid, of suspended particles which are large compared with the molecules of the liquid has been worked out in detail by Einstein*. But the extended theorem of the virial permits of the immediate extension of some of the gas-laws to suspended particles in Brownian motion without further consideration.

Each particle, assumed to be spherical, is acted on by a frictional force proportional to its velocity and to the viscosity of the liquid. The precise value of the resistance is given by Stokes's law. But we now see that when the suspension is in a steady state the forces due to viscosity can be left out of account in calculating the virial, and hence the properties of a gas depending on the virial apply as they stand to the suspended particles.

* *Ann. der Phys.* xi. p. 170 (1903); xix. p. 372 (1906).

We consider the system of suspended particles only. Let P be the part of the pressure on the walls of the containing vessel due to the suspended particles. By a well-known calculation, the contribution to the virial of the forces arising from the walls of the vessel is

$$\tfrac{1}{2}\mathrm{P}\iint(lx+my+nz)\,d\mathrm{S},$$

l, m, n being the direction cosines of the outward normal, and the integral being extended over the walls. If V is the total volume, this is equal to

$$\tfrac{3}{2}\mathrm{PV}.$$

If the concentration is sufficiently small, the contribution to the virial due to pairs of particles in collision can be neglected. If each suspended particle were acted on only by the viscous resistance calculated by Stokes's formula, it would soon be brought to rest, and there would be no steady state. Actually there is another contribution to the force, due to the fluctuations in motion of the surrounding molecules of the liquid, and these suffice to keep the particles statistically in a steady state. It is easily seen that the contribution to the virial of the random part of the resistance is zero. Omitting the systematic part depending on the velocity, by the theorem, we have

$$\tfrac{3}{2}\mathrm{PV} = \Sigma\tfrac{1}{2}\overline{mv^2}.$$

This shows that the partial pressure P of the suspended particles obeys the gas-laws. A similar calculation gives the law of osmotic pressure for dilute solutions in general.

Though frictional forces act on the suspended particles, there is no "dissipation" of their energy. The particles communicate kinetic energy to the molecules in virtue of their motion of translation through the liquid, but this is on the average returned to the particles owing to the irregular motions of the molecules they collide with. As Clausius said, the theorem of the virial is a mechanical theorem applicable to heat, and kinetic energy turned into heat is fully accounted for.

IV. *The pressure of radiation on the molecules of a gas which is in a steady state.*

Consider an enclosure at temperature T containing a gas in a steady state. The enclosure will be filled with black radiation of temperature T, and each molecule will be absorbing and emitting the frequencies corresponding to its energy levels. For a molecule at rest, the absorption of

energy will be the same in all directions, and emissions will be equally distributed in direction. Thus, on the average, there will be no gain of momentum due to absorptions, and no gain of recoil momentum due to emissions. The molecule experiences no net pressure of radiation.

But for a molecule in motion, the field will no longer be isotropic to an observer moving with the molecule. Radiation will be more intense in the direction opposite to that of the motion. Consequently there will be an excess of absorptions of oppositely moving radiation, and hence a net gain of momentum in a direction tending to reduce the velocity to zero. To the first order in v, the effect is that of a frictional force proportional to v. The absolute value of the force has been calculated by Einstein *. Here, however, we simply point out that the circumstances are analogous to those for Brownian motion †. By the extended theorem of the virial, the effect of the pressure of radiation can be ignored, and thus all consequences of the virial theorem which hold in the absence of radiation hold also when radiation is taken into account.

Trinity College, Cambridge,
April 1925.

XLI. *Optical Screening-Constant Regularities.* *By* A. C. Menzies, *M.A., Lecturer in Physics, The University, Leeds* ‡.

Introduction.

RECENTLY Millikan and Bowen (1) have applied certain X-ray laws to optical spectra, and in particular have used the relativity-doublet formula $\partial\nu = K(Z-s)^4$ to express the relationship between doublet-separation in wave-numbers (ν) and the atomic number (Z), the screening-constant s having a value which is adjusted. K is a constant varying inversely as the cube of the total quantum-number, and has for $n=2$ (*e.g.* in the innermost Li series-electron levels) the value 0·365. Applied to lithium-like atoms, the screening-constant had values ranging from 2·02 for Li I to 1·86 for C IV.

* *Phys. Zeit.* xviii. p. 121 (1917).
† Einstein pointed out this analogy in calculating the force.
‡ Communicated by Prof. R. Whiddington, F.R.S.

The same formula was applied to triplets by treating the wider separation as that of a doublet; since in triplets the term-separations have a simple numerical ratio (*e.g.* the *p*-terms of the elements of group II, 2 : 1), taking instead the total separation will merely alter $(Z-s)$ in a constant ratio.

The formula is here applied generally to optical doublets and triplets, a value of s being obtained characteristic of the atom with its valency electron in the particular orbits concerned. Simple numerical relationships are then found between the screening-constants for elements in the same vertical group of the periodic table.

As might be expected, seeing that they have similar electronic configurations, there is a simple connexion between the values of s calculated for the arc spectra of the alkali metals and for the spark spectra of the corresponding alkaline earths. The values of s for the alkaline-earth spark spectra are approximately nine-tenths those belonging to the corresponding elements of the alkali metals, as is shown in Table I. following :—

TABLE I.

Atom.	s.	Atom.	s.	Ratio.
Li I	2·019	Be II ...	1·937	0·96
Na I	7·448	Mg II ...	6·606	0·89
K I	13·03	Ca II ...	11·64	0·89
Rb I.....	26·96	Sr II ...	24·37	0·90
Cs I.....	40·77	Ba II ..	37·19	0·91
Cu I	20·41	Zn II ...	18·24	0·89
Ag I.....	32·92	Cd II ..	29·95	0·91
Au I.....	55·94	Hg II ...	50·8	0·91

The values of s in the above table are calculated from the separations $(2p_2-2p_1)$ for Li I and Be II, and for corresponding separations in the other elements.

There seems also to be a similar relationship holding between the values of s obtained for np orbits compared with $(n+1)p$ orbits for the alkali metals :—

TABLE II.

Element.	s.	s_1.	Ratio.
Na	7·448	7·858	1·055
K.....	13·03	13·57	1·042
Rb	26·96	28·30	1·050
Cs	40·77	42·92	1·053

In the second column are the values of s calculated from the first separation in the principal series, and in the third column s_1 is that calculated from the second separation—*i. e.* for Li $(2p_2-2p_1)$ and $(3p_2-3p_1)$ respectively.

The above two tables suggest that there is more than coincidence in the values obtained by applying the relativity formula to optical doublets, and so further relationships were sought.

Screening-Constants and Atomic Numbers.

The screening from the nucleus which an electron suffers because of the remaining electrons in the atom will be greater the greater the total number of electrons; and in considering atoms of elements of the same vertical group of the periodic table, it seemed reasonable to test whether the effective screening of corresponding orbits was proportional to the atomic numbers. It was found (2) that the screening-constants were, in fact, nearly linear with atomic number for all the groups tried. The divergence is more marked for small atomic numbers, as would be expected, since other factors than the total number of electrons contribute to the screening-constant; but for sub-groups such as K, Rb, Cs (1 per cent. out), Ca, Sr, Ba ($\frac{2}{3}$ per cent. out), and Mg II, Ca II, Sr II, Ba II (Ra II is 2·3 per cent. out) the divergence is small.

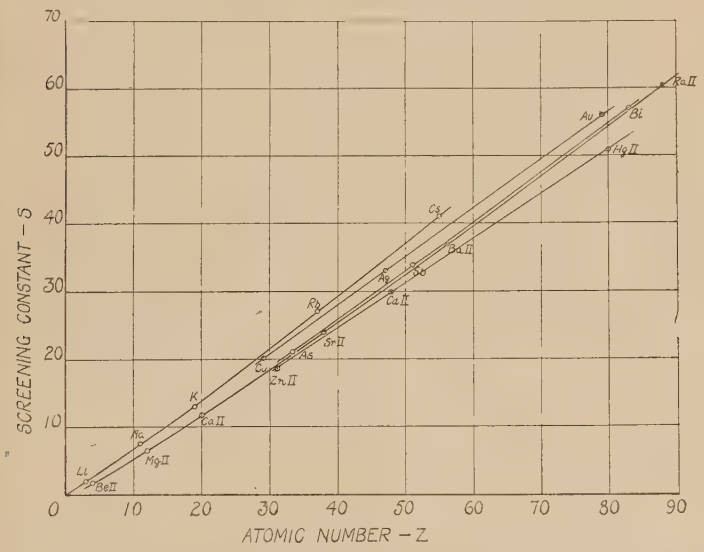
Screening-constants may therefore be usefully employed in arriving at a number of the right order for the separations of doublets and triplets previously unrecognized or unassigned to their atoms. For example, it can be shown that the separations 3815 and 9829 are probably correct for Au I and Hg II respectively, since they give screening-constants in line with those for Cu I and Ag I, and those for Zn II and Cd II respectively. Moreover, their values for s are in the right ratio (see Table I.).

Again, a screening-constant 7·163 for Al II calculated from Paschen's doublet separation (3) is nearly in line with 16·2 and 24·86 for Ga II and In II respectively, calculated from frequency differences found in tables of wave-lengths given by Weinberg recently (4). These frequency differences have enabled the writer to deduce series for Ga II and In II, but they are withheld for experimental confirmation.

It is tempting to extrapolate for the Ra arc separation; the probable value, 64·12, for the screening-constant would indicate about 2800 for the wider separation. The separations and lines at present attributed to this spectrum are unsatisfactory; Hicks (5) finds separations 2050 : 832, and Anslow

and Howell (6) get 2017 : 1036. These give totals 2882 and 3053. The separation at present regarded as the total separation may in reality be the wider separation.

To show the kind of relation which exists between s and z a graph is given, having atomic numbers as abscissæ, and as ordinates screening-constants calculated as explained above. These curves are to be taken as typical. The alkali-metal curve is for s calculated from the term separations $(2p_2-2p_1)$(Li), and so also is the alkaline-earth spark-line. The curve for As, Sb, and Bi is for screening-constants calculated from the



term separations $(3D_2-3D_1)$ as given by Ruark and others (7).

This curve should really lie much closer to the curve for Sr II, Ba II, Ra II, but it has been raised slightly to show that the two are separate in the reproduction.

It will be observed that all the lines have much the same slope.

Change in S *with Building-up of Atoms.*

If the elements are considered in the order of their arrangement in vertical groups of the periodic table, they may be imagined to be built up by the successive additions of rings of electrons containing either 8, 18, or 32. Now it is noticeable that for all the groups, increase in the atomic

number of 8, 18, or 32 corresponds to an increase in s of about 5, 13, and 23. This is well shown by the elements of group I arc, II arc and spark, and III b arc, as in Table III.

TABLE III.

Element.	Z.	dZ.	dS.	Element.	Z.	dZ.	dS.	Element.	Z.	dZ.	dS.
Li I ...	3	8	5·43					Be II ..	4	8	4·123
Na I..	11	8	5·58	Na I...	11	18	12·96	Mg II..	12	8	5·58
K I ...	19	18	13·94	Cu I...	29	18	12·51	Ca II ..	20	18	12·73
Rb I...	37	18	13·80	Ag I...	47	32	23·02	Sr II ..	38	18	12·82
Cs I ...	55			Au I...	79	(18)	(12·95)	Ba II ..	56	32	23·33
								Ra II ..	88	(18)	(13·12)

Element.	Z.	dZ.	dS.	Element.	Z.	dZ.	dS.	Element.	Z.	dZ.	dS.
Mg II..	12	18	12·18	B I ...	5	8	4·881	C II...	6	8	4·53
Zn II ..	30	18	11·71	Al I ...	13	18	12·07	Si II...	14		
Cd II ..	48	32	20·85	Ga I...	31	18	12·06	N III..	7	8	4·24
Hg II..	80	(18)	(11·73)	In I ...	49	32	21·98	P III ..	15		
				Tl I ...	81	(18)	(12·36)				

Element.	Z.	dZ.	dZ.	Element.	Z.	dZ.	dS.
Be I ...	4	8	5·18				
Mg I ..	12	8	5·47	Mg I ..	12	18	12·80
Ca I ...	20	18	13·55	Zn I ..	30	18	12·66
Sr I ...	38	18	13·46	Cd I ..	48	32	22·75
Ba I ...	56			Hg I ..	80	(18)	(12·78)

At the same time the differences illustrate to what extent s is linear with Z. Numbers in brackets have been calculated for an addition of 18 instead of 32 electrons, assuming proportionality.

It will be observed that, for the first two groups, the increments of s cluster round the values 5·4, 13·2, and 23 for additions of 8, 18, and 32 electrons respectively. This suggests that additions of these numbers of electrons in the outer regions of the cores are as effective as a reduction in

the nuclear charge of amounts given by the values of s above.

Now in the case of a penetrating orbit, we might expect that addition of electrons in the outer part of the core would have most effect in the part of the orbit of the valence electron in this region or outside it. Consequently, since the innermost part of the orbit is approximately the same for different elements in the same column, we can form a rough estimate of the *change* in s to be expected from means in the screening while the electron is in this region and outside it. When eight electrons are added, the difference in s will be 8 for the electron outside the ring, while, if in the ring, the difference would be 3·3.

This gives as an average 5·7, while the average for group I arc and group II spark is 5·2 (these were chosen as being the simplest). Again, for 18 electrons the effective nuclear charge will diminish by 18 while the electron is outside, and by 9·3 while in the region of the ring, giving as an average 13·6. Lastly, for 32 electrons the change to be expected calculated in the same manner is 25.

Such averaging has little physical justification, and has been adopted only in order to gain some estimate of the order of change in screening to be expected. The crude idea of rings has, of course, given way to the more plausible one of separate orbits ; but it can evidently still be usefully employed to obtain rough numerical estimates.

Variation in dS *with* n *in the same Atom.*

The greater the penetration of an orbit into the core the less will be the screening, and so the greater will be $(Z-s)^4$, and so the greater also will be the corresponding separation. Deep penetration can therefore be connected with large separations, and small separations can be taken to be a symptom of shallow penetration. (Different orbits of the *same atom* are in mind.) Thus we might expect that if for any atom $\Delta d > \Delta p$, the d orbits penetrate more deeply into the core than the p orbits. Furthermore, the less penetrative the orbit the greater might Δs be, going down a group ; for since in the procession from Li to Cs rings of 8, 8, 18, 18 electrons are added in turn, if the valence electron was entirely outside the core all the time, s would change by 8, 8, 18, 18 units at a time respectively. Table IV. shows how s and Δs increase for more distant orbits—*i. e.* as n increases for the same series of terms.

TABLE IV.

(*a*) Arc Spectra, Alkalies.

Element.	s.	s_1.	Δs.	Δs_1.
Na	7·45	7·858	5·58	5·711
K	13·03	13·57	13·94	14·73
Rb	26·97	28·30	13·80	14·62
Cs	40·77	42·92		

(*b*) Spark Spectra, Alkaline Earths.

Element.	s_1.	s_2.	s_3.	Δs_1.	Δs_2.	Δs_3.
Mg	6·06	10·27	...	5·58	3·68	...
Ca	11·64	13·96	14·65	12·73	13·58	14·42
Sr.....	24·37	27·54	29·07	12·82	12·86	14·48
Ba	37·19	40·4	43·55	23·33	...	27·27
Ra	60·52	...	70·82			

In the above table, s and s_1 apply to $(3p_2-3p_1)$ and $(4p_2-4p_1)$ for Na etc., and s_1, s_2, s_3 to $(3p_2-3p_1)$, $(3d_2-3d_1)$, and $(4d_2-4d_1)$ respectively for Mg etc. The change Δs_2 of 3·68 between Mg and Ca is not in agreement, and suggests that very little penetration occurs in this orbit in the case of Mg, since s_2 for this element is abnormally high.

(*c*) Arc Spectra, Earths.

Element.	s_1.	s_2.	s_3.	s_4.	Δs_1.	Δs_2.	Δs_3.	Δs_4.
Al	7·326	8·726	9·01	9·18	12·07	14·03	14·57	14·78
Ga	19·4	22·76	23·58	23·96	12·06	14·12	14·73	15·06
In.....	31·46	36·88	38·31	39·02	21·98	25·60	26·70	27·39
Tl.....	53·44	62·48	65·01	66·41				

s_1, s_2, s_3, s_4 in the above are screening-constants calculated from the separations $(3p_2-3p_1)$, $(4p_2-4p_1)$, $(5p_2-5p_1)$, and $(6p_2-6p_1)$ respectively in the case of Al, and similarly for the other elements.

Optical Multiplets are Magnetic rather than Relativistic.

In the foregoing the relativity doublet formula of Sommerfeld has been applied to optical separations, the screening-constant s being used as an adjustable quantity. It has been shown that in passing down a chemical group the screening-constant increases in a way to be expected if the more complex atoms are formed from the preceding ones by addition of rings of 8, 8, 18, 18, and 32 electrons. The formula applied was obtained by Sommerfeld by consideration of the relativity variation of mass with velocity, which will introduce different changes in the energy of orbits of the same total but different azimuthal quantum numbers. There is, however, a large amount of experimental and theoretical evidence derived from a study of the anomalous Zeeman effect to support the view that these multiplet separations are magnetic rather than relativistic in origin, being due to internal atomic magnetic fields.

In the case of a penetrating orbit, the part of the orbit which will contribute most to the relativity effect will be that part where the electron is moving fastest—that is, at the perihelion. This will probably also be true for the magnetic effect, since near the perihelion the electron will be moving fastest, and will therefore be under the influence of greater forces due to the magnetic fields. Thus it is plausible that the screening-constants calculated from a relativity formula should have values in accordance with what is really a magnetic phenomenon.

In its fuller form, K is $\frac{\alpha^2 \mathrm{R}}{n^3}\left(\frac{1}{k} - \frac{1}{k'}\right)$, and applies to orbits having the same n's but different k's. In the above it has been applied to orbits having the same n and k but different j's. As used, $\mathrm{K} = \frac{\alpha^2 \mathrm{R}}{2n^3}$.

It may be noted that an expression of the form $\frac{\alpha \mathrm{R}}{n^3}\left(\frac{1}{j} - \frac{1}{j'}\right)$ for K would give correct ratios for the separations if particular values of j were used ; but the wider separations would then be associated with the smaller inner quantum numbers instead of with the larger ones. This seems a fatal objection to any such formula. The entering of the j's in the form $(j+j')$, as proportional to the intervals, shows no analogy with the relativity formula.

Closeness of Agreement.

The numerical relationships outlined above depend upon a fourth-power law. This causes the apparent agreement to be greater than it really is, as, on taking the fourth root of the separation, discrepancies are naturally divided by four.

On the other hand, prophecy is made more uncertain, since a screening-constant which has been predicted for an atom in a particular condition must be raised to the fourth power; and so the expected separation lies within a range which has been multiplied four-fold.

References.

Except where otherwise stated, separations used are those given in Fowler's Report on Spectra;
Paschen-Goetze, 'Seriengesetze der Linienspektren';
or Hick's 'Analysis of Spectra.'

(1) Millikan and Bowen, Phys. Rev. xxiv. pp. 209–222.
(2) 'Nature,' cxiv. p. 861 (1924).
(3) Paschen, *Ann. der Physik*, lxxi. p. 537 (1924).
(4) Weinberg, Proc. Roy. Soc. A, cvii. p. 138 (1925).
(5) Hicks, Phil. Trans. A, ccxii. p. 64 (1913).
(6) Anslow and Howell, Proc. Nat. Acad. Sci. Wash. iii. p. 409 (1917).
(7) Ruark, Mohler, Foote, and Cherault, U.S. Bureau of Stds. Sci. Paper 490 (1924).
(8) Sommerfeld, 'Atomic Structure,' English edn. p. 76.

Summary.

(1) Screening-constants have been calculated for the optical doublets and triplets of several chemical groups of atoms by application of the relativity doublet formula.

(2) In passing down a chemical sub-group of the periodic table the screening-constant is found to vary directly as the atomic number.

(3) For many such sub-groups the change in s has approximately constant values in passing from one element to the next; for $Z=8$, 18, 32 s is nearly 5, 13, 23 respectively.

(4) These numbers are shown to be of the order to be expected on simple considerations.

(5) The significance of the formula is discussed in the light of the probability that the origin of multiplets is magnetic rather than relativistic.

Physics Laboratories,
The University, Leeds,
May 1925.

XLII. *Potassium as a Mercury-Vapour Trap* By A. Ll. Hughes, *D.Sc.*, *and* F. E. Poindexter, *M.A.*, *Washington University, Saint Louis, U.S.A.* *

Introduction.

As is well known, the speed and simplicity of the mercury-vapour condensation pump has led to its almost universal adoption in the production of extremely high vacua. It suffers from the disadvantage that, while it rapidly removes gases and vapours from the vessel to be exhausted, it does not remove mercury vapour. To stop the mercury vapour from diffusing back into the apparatus, the usual practice is to have a trap which can be surrounded by liquid air between the pump and the apparatus to be exhausted. The cost of making liquid air, the difficulty of getting it in certain laboratories, and, in some researches, the need for keeping the mercury trap in action for some weeks without a break, suggested the desirability of looking for some alternative method. The present paper is the outcome of a search for a substitute for liquid air. Years ago, gold-leaf was used to prevent mercury vapour passing a certain point in a vacuum system, but apparently without much satisfaction. During the last two years, we have re-investigated the possibility of metals as mercury-vapour traps. The most surprising result of this investigation is the amazing ability of the alkali metals to absorb mercury vapour. For practical purposes, it is fair to say that the diffusion of mercury vapour past a certain region in a vacuum system is stopped by lining a trap with an alkali metal quite as satisfactorily as by cooling the trap with liquid air.

An account of an investigation on sodium as a mercury-vapour trap has been published by one of us †. In the present paper we give the results of a detailed investigation on the use of potassium as a means for preventing mercury vapour diffusing through a vacuum system. Two methods of investigation were adopted. In the first, we used a qualitative spectroscopic test to determine for how many weeks a lining of potassium inside a tube would remain an effective barrier to mercury vapour. In the second method we used ionization gauges to determine the lowest pressures attainable under our various experimental conditions.

* Communicated by the Authors.

† F. E. Poindexter, Jour. Optical Soc. America, ix. p. 629 (1924).

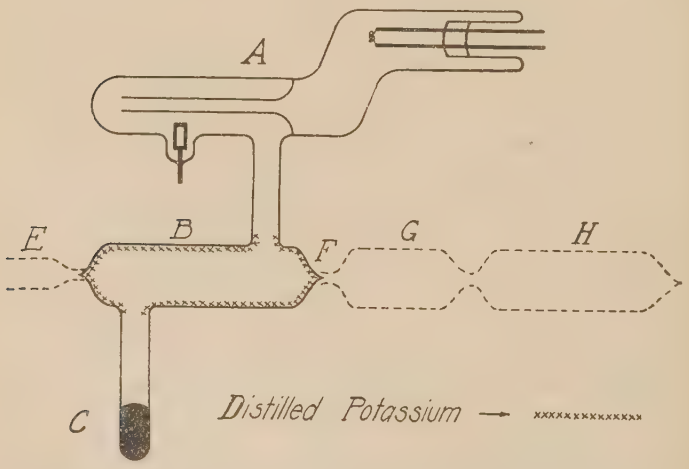
Spectroscopic Tests.

In these tests, use is made of the fact that a small trace of mercury vapour in a discharge-tube is shown by the appearance of mercury lines in the spectrum of the discharge. It has been suggested that, in a mixture of gases, the spectrum of the gas with the highest ionizing potential is relatively less strongly excited than that of the gas with the lowest ionizing potential. It is therefore to be expected that, in a spectroscopic test, traces of mercury would show up more strongly in helium than in other gases. Whether this be true or not, helium has certain other advantages : it is easy to obtain in pure form, and gives a spectrum in which the presence or absence of mercury lines can be determined without ambiguity.

Apparatus.

The apparatus used is shown in fig. 1, which is approximately to scale. It consists of three parts, a discharge-tube, A, the potassium-lined trap, B, and a mercury reservoir, C.

Fig. 1.



The discharge-tube is of the internal capillary type (diameter 3 mm.) which can be viewed end-on. One electrode is a tungsten filament which can be made incandescent to increase the intensity of the discharge if necessary. The mercury reservoir is a tube 11 mm. in diameter and contained 52 grams of mercury. A mark on the outside of the tube indicates the height of the mercury when first put in. The amount which evaporated and had been absorbed by the

potassium in the course of time could be determined from the depression of the surface of the mercury below this mark. The distance from the surface of the mercury to the horizontal tube B was about 7 cm. The apparatus was connected to a diffusion pump through E. A small piece of newly cut potassium weighing 2·5 grams was inserted into the part H, the end of which was then sealed off as soon as possible. The pumps were then started, and when a good vacuum was obtained the whole apparatus (except the mercury reservoir and the tube H containing the potassium) was heated by a hand blowpipe for about one hour. After cooling, the potassium was first distilled into G and finally into B. When this had been done, G and H were sealed off at F. The potassium was distributed in a thin layer, no doubt unevenly, over the inside of the tube B, the exposed surface area being approximately 30 sq. cm. Owing to slight oxidation on introducing the potassium into the apparatus, the amount of potassium lining the tube B was certainly somewhat less than 2·5 grams, this being the amount of potassium originally put in. A small quantity of helium, purified by passing slowly through charcoal in liquid air, was then admitted to the apparatus, the McLeod gauge showing a pressure of ·01 mm.

Method of Experiment.

The spectrum was excited by a 10,000 volt transformer. During the first few observations it was unnecessary to heat the filament. Soon, however, the tube had hardened to such an extent that it was necessary to make the filament hot to get a discharge to pass. The cause of this diminution in pressure is not known, but we may consider that it made the tests more stringent in that the amount of helium, available for carrying the discharge, was less than before in comparison with possible traces of mercury. The spectrum was examined visually by means of a Hilger constant deviation spectrometer, and a careful search made for the principal mercury lines. The spectrum was also photographed, the exposures being such that the helium spectrum was much overexposed to give every chance for the appearance of mercury lines should there be present any trace of mercury.

Results.

After the apparatus had been sealed off from the pump, the spectrum was examined at frequent intervals (at first

every week, then less often). Even when the discharge was so strong as to make the helium spectrum very bright, there was not the slightest trace of any mercury lines to be seen, either visually or photographically, until the eleventh week after the tube had been sealed off. Then, and only then, was there any indication of mercury in the spectrum. Along with a very bright helium spectrum, we could see with difficulty the green line of mercury (λ5461) but no other mercury lines at all. A photograph, much over-exposed so far as the helium spectrum is concerned, showed the lines λ4358, λ4047, and λ3663, faintly, but nothing of the green line λ5461. By this time, the lowering of the level of the mercury in the tube C showed that 3·7 grams of mercury had evaporated and had been absorbed by less than 2·5 grams of potassium. After the eleventh week the mercury spectrum increased very slowly in intensity until the twenty-first week, when the mercury spectrum was plainly visible (this being the last observation made). At this stage, 13 grams of mercury had been evaporated and taken up by the potassium.

This test clearly shows that a comparatively small quantity of potassium spread out in a thin layer acts as an efficient mercury-vapour trap and that it retains its power for a long period. It should be pointed out that this test is unusually drastic in that the source of mercury is very much closer to the trap (7 cm.) than it would be in most experimental arrangements. The amount of mercury vapour diffusing into the trap per second is inversely proportional to the distance from the source to the trap and directly proportional to the cube of the radius (assuming for simplicity that the mean free path of the mercury atoms is greater than the diameter of the tube). This being so, we may reasonably assume that had the mercury been in a tube of the same diameter, but at a distance of say 40 cm. from the trap, it would have taken about a year before traces of mercury vapour would have appeared in the spectrum.

It will be noticed that the potassium continues to act as an efficient barrier to the passage of mercury vapour until it has absorbed over 150 per cent. of its own weight of mercury.

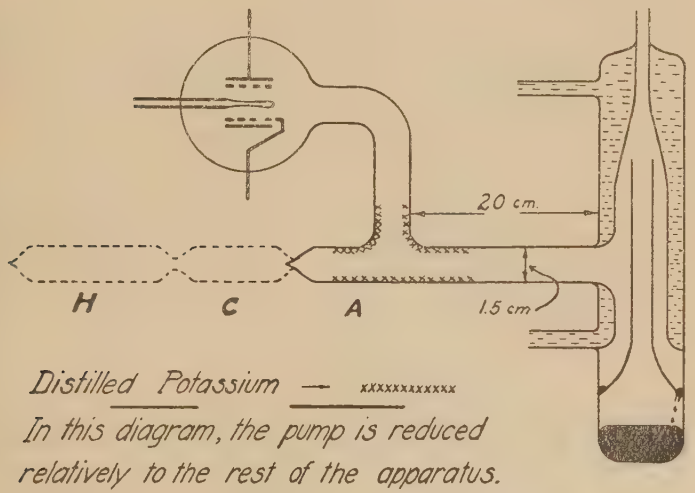
Ionization Gauge Tests.

First Ionization Gauge.

The arrangement used in this test is shown in fig. 2. The path between the ionization gauge and the condensation pump is short and wide so as to give the pump every chance

to remove the gases as completely as possible. It also shows what is perhaps as simple and convenient a form of alkali metal trap as can be made. There is no need to describe the ionization gauge as it is of the usual type *. It is sufficient to say that it is a three-electrode tube in which the positive ion current produced by impact of electrons on the residual gas or vapour molecules can be measured. At low pressures, the pressure is proportional to the ratio of positive ion current to the electron current. The gauge was calibrated before this test by inserting a U tube between it and the

Fig. 2.



diffusion pump. The U tube contained a few drops of mercury but not enough of course to close the tube. The U tube was surrounded by melting ice and the ratio of the positive ion current, P, to the electron current, E, was measured with the diffusion pump in action. Under these conditions the only gas or vapour left in the ionization gauge was mercury vapour. According to Knudsen †, the vapour pressure of mercury at 0° C. is $1{\cdot}88 \times 10^{-4}$ mm. We found the ratio of the positive ion current to the electron current with mercury vapour at 0° C. to be

$$(P/E)_{0°C.} = 6{\cdot}64 \times 10^{-3}.$$

* O. E. Buckley, Nat. Acad. Sci. Proc. ii. p. 683 (1916). S. Dushman, Physical Review, xvii. p. 7 (1921). F. E. Poindexter, Jour. Opt Soc. America, ix. p. 629 (1924).

† Knudsen, *Ann. d. Phys.* xxix. p. 179 (1909).

After this preliminary calibration the gauge was set up as shown in fig. 2. A small piece of potassium, approximately 3 grams, was inserted into the tube H and the end sealed off. Then the pump was started and the gauge and connecting tubes (except H) were heated vigorously for an hour or two by a hand blowpipe to drive gases off the walls. Then for a period of two or three hours the anode was outgassed at a red heat by electronic bombardment. Meanwhile the potassium in H was heated at gradually increasing temperatures to drive off gases and then distilled into C and finally into A. The distribution of the potassium is indicated in the diagram. The tubes H and G were now sealed off. The ionization gauge was again outgassed by the hand blowpipe and the anode by electronic bombardment. After cooling, the ratio of the positive ion current to the electron current was again measured and found to be

$$(P/E)^K = 2 \times 10^{-7}.$$

The positive ion current was now so small as to correspond to less than a scale-division deflexion, hence the ratio cannot be determined accurately. However, the vapour pressure of the mercury in the ionization gauge with the potassium trap in action has been reduced to

$$\frac{2 \times 10^{-7}}{6{\cdot}64 \times 10^{-3}} = 3{\cdot}0 \times 10^{-5}$$

times its value at 0° C.

Now, at 0° C. according to Knudsen, the vapour pressure of mercury is $1{\cdot}88 \times 10^{-4}$ mm. Consequently the vapour pressure of mercury in the ionization gauge with the potassium acting as a trap is equal to, or less than

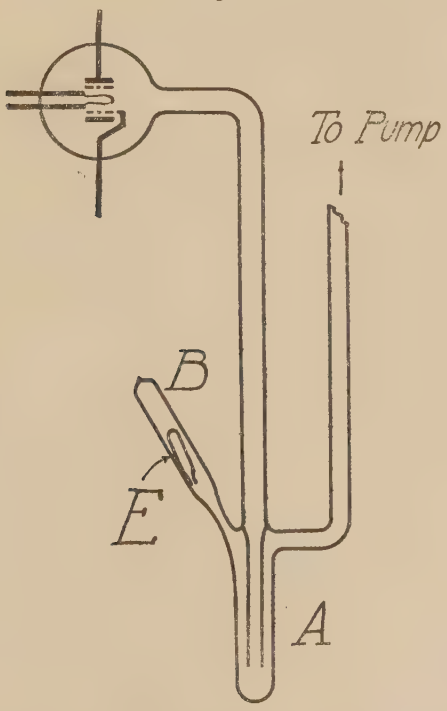
$$(1{\cdot}88 \times 10^{-4}) \times (3{\cdot}0 \times 10^{-5}) = \underline{5{\cdot}6 \times 10^{-9}\ \text{mm.}}$$

It should be emphasized that this is an *upper limit*. We do not know that the gas or vapour whose pressure we are measuring is mercury vapour at all, but we do know that if it is all mercury vapour then its pressure does not exceed $5{\cdot}6 \times 10^{-9}$ mm. It is quite likely that, even after the heat treatment we gave to the gauge, minute quantities of gas are slowly being evolved from the walls, anode, and filament, and that what we measure depends on the equilibrium between the rate of evolution of such gases and the rate of removal by the pump. Hence we may justifiably conclude that the efficiency of a potassium trap as a barrier to mercury vapour is such that the pressure of mercury vapour beyond the trap can be reduced to less than 5×10^{-9} mm.

Second Ionization Gauge.

The second ionization gauge was set up in such a way as to enable us to make a direct comparison between the effect of a potassium trap and that of a liquid-air trap. It was also convenient for investigating whether contact of air with the potassium reduced its power as a mercury trap. This apparatus is shown in fig. 3. The tube between the gauge and the trap was 100 cm. long and 2 cm. in diameter, and that between the trap and the pump was 250 cm. long and 1·2 cm. in diameter.

Fig. 3.



The experiments to be described show that a potassium trap is as efficient as a liquid-air trap. The apparatus was outgassed by a hand torch and the anode was made red hot by electronic bombardment for about an hour. Then the part A was surrounded by cold water at 1°·8 C. The ratio of the positive ion current, P, to the electron current, E, was found to be

$$(P/E)_{1°\cdot8\,C.} = 3\cdot28 \times 10^{-3}.$$

(This was not the same ionization gauge as that used in the preceding section.) At 1°·8 C. the vapour pressure of mercury is $2{\cdot}19\times10^{-4}$ mm. The next step was to surround A by liquid air, making it into the usual liquid-air trap. The outgassing treatment consisted of heating all the exposed tubes and the gauge itself with a hand blowpipe for a period of one hour and heating the anode to a red heat by electronic bombardment for two hours. After everything had cooled the ratio of the positive ion current to the electron current was measured and found to be

$$(P/E)_{\text{liquid air}}=2{\cdot}3\times10^{-6}.$$

The reduction in pressure is therefore to

$$\frac{2{\cdot}3\times10^{-7}}{3{\cdot}28\times10^{-3}}=7{\cdot}0\times10^{-4}$$

of its value at 1°·8 C. This gives for the actual pressure a value of

$$(2{\cdot}19\times10^{-4})\times(7{\cdot}0\times10^{-4})=143\times10^{-9}\text{ mm.}$$

The next step was to remove the liquid air and to admit air up to atmospheric pressure into the gauge and pumping system. A small open bottle containing 1 gram of potassium was inserted into B. The pumps were then started and the apparatus was outgassed as before. Heat was applied to the potassium until it melted and ran down into the bottom of A. From here by cautious application of a small flame it was distilled so as to cover the inside of the upper part of A in a thin layer. The outgassing treatment before and after distilling the potassium was carried out in exactly the same way and for the same length of time as was done before and after surrounding the trap with liquid air in the earlier experiment, so as to make the experiments as comparable as possible. After the outgassing was finished the ratio of the positive ion current, P, to the electron current, E, was found to be

$$(P/E)_{K}=1{\cdot}2\times10^{-6}.$$

Proceeding as before, this gives for the actual pressure a value of

$$\left\{\frac{1{\cdot}2\times10^{-6}}{3{\cdot}28\times10^{-3}}\right\}\times2{\cdot}19\times10^{-5}=74\times10^{-9}\text{ mm.}$$

These results show clearly that with the kind of outgassing treatment given to the apparatus a potassium trap is at least as good as a liquid-air trap. That it appears to be actually twice as good is no doubt due to the fact that

the potassium test came *after* the liquid-air test and therefore the apparatus was in a better outgassed condition, even though in between the two experiments air at atmospheric pressure had been admitted to the apparatus for about an hour. We have frequently noticed in the course of our work that a well outgassed apparatus retains much of its outgassed condition even after admitting air to atmospheric pressure for several hours.

After a further outgassing treatment lasting two hours, the pressure dropped to 56×10^{-9} mm.

It should be emphasized again that we do not consider the values here recorded to be real vapour pressures of mercury. They are upper limits, probably many times greater than the true values. They doubtless indicate that, even after considerable outgassing, gas is slowly given off by the walls, anode, and filament, and being removed by the pump. On this view, the lower pressure attained with the first ionization gauge is naturally interpreted as being due to the fact that, on account of the much shorter distance from the gauge to the pump, the evolved gases are removed much more effectively, with the result that a lower equilibrium pressure is attained.

Effect of Admitting Air.

As it is suggested that in many investigations requiring a high vacuum an alkali metal may be used instead of liquid air as a mercury-vapour trap, it is necessary to examine how sensitive the potassium surface is to the effect of gases, and, in particular, to dry air and ordinary air. It is of course obvious that the practical usefulness of potassium as a mercury-vapour trap would be much diminished if exposure to a trace of air destroyed its trapping power. The following tests were carried out.

First Air Test.

Air was passed slowly through phosphorus pentoxide into the apparatus until atmospheric pressure was obtained. About two litres of air at atmospheric pressure passed by the potassium. The effect of the dry air on the surface of the potassium was very marked. The silvery bright surface immediately turned black when air was admitted. After contact with the dry air at one atmosphere pressure for one hour, the air was pumped out again to a pressure below the limit of the McLeod gauge. Next morning the dull black surface of the potassium had become grey and granular. The pump was started again, and the gauge

and tubes were now outgassed by heating with the hand blowpipe for twenty minutes, and the anode raised to a red heat by electronic bombardment for thirty minutes. The potassium was of course not heated in any way. The pressure obtained after everything had cooled was 38×10^{-9} mm., and after ninety minutes of continuous pumping it fell to 28×10^{-9} mm.

Second Air Test.

Without renewing the potassium surface in any way, the procedure in the first test was again repeated. Dry air was admitted to atmospheric pressure, and, after one hour, it was pumped out again. Next morning the pump was started, and the outgassing consisted of electronic bombardment of the anode for one hour, but without heating the glass with the blowpipe. The pressure obtained was again 28×10^{-9} mm.

Third Air Test.

The sequence of operations here was exactly the same as in the second test, and the pressure obtained was about 30×10^{-9} mm.

Fourth Air Test.

We now admitted room air without any special drying, and left it in for thirty minutes before beginning to pump it out. Then the apparatus was heated by a blowpipe flame for thirty minutes and the anode by electronic bombbardment for two hours. The pressure reading obtained immediately after this was 210×10^{-9} mm. Next morning, without any further treatment beyond outgassing the anode by electronic bombardment for one hour, the pressure was found to be 60×10^{-9} mm. The blowpipe flame was now played over the ionization gauge and tubes for thirty minutes, with the result that the pressure fell to 30×10^{-9} mm.

It is to be noticed that the final pressure obtained at the end of the fourth air test was practically as low as that obtained at any time during or before the admission of air. In the course of these tests approximately eight litres of air (six litres of dry air, two litres of room air) were passed over the same potassium surface without affecting its efficiency as a mercury-vapour trap. This is somewhat surprising, as one might reasonably have expected the dull coating formed over the potassium surface to destroy its ability to take up mercury vapour.

Fifth Air Test.

To examine further the effect of room air as contrasted with dry air, the following test was made. Room air was admitted to atmospheric pressure, allowed to stand for about half-an-hour, and pumped out again. This procedure was repeated three times, so that altogether about six litres of room air had passed over the potassium surface. The apparatus was then pumped out and left overnight. Next day, the potassium was heated for a short while to re-distribute it over the inside of the trap. The outgassing of the gauge and connecting tubes consisted in heating them with the blowpipe flame for thirty minutes and heating the anode by electronic bombardment for about one hour. After this, the pressure gradually fell to 10×10^{-9} mm., the lowest yet obtained with this gauge.

Sixth Air Test.

Most of the foregoing pressure measurements were made on the morning following the day on which the air was admitted. It is desirable to put on record a result which shows the effect obtained when the procedure is hurried. Room air was admitted to atmospheric pressure and allowed to stay for about an hour. It was then pumped out, and as soon as the pressure was hardly noticeable on the McLeod gauge, the potassium was redistributed in the trap by heat, and the gauge and the apparatus were outgassed by the hand blowpipe for fifteen minutes and the anode was brought to a red heat by electronic bombardment for ten minutes. The ionization gauge soon afterwards showed a pressure of 115×10^{-9} mm., this observation being made within thirty-five minutes from the time the diffusion pump came into action. The pressure fell slowly as the pumping proceeded. No doubt it would have reached as low values as were obtained in previous tests, had the apparatus been given further outgassing treatment, but this was not actually demonstrated at the end of this particular test.

Attention is called to the fact that the same one gram of potassium was used in all these tests, and that its power for trapping mercury was not in the least impaired by the passage over it of about twelve litres of air in all. In fact, at the completion of all these tests, the apparatus was opened, and certain alterations made in preparation for an entirely different research. The apparatus was then sealed and exhausted and outgassed, and a pressure of 10×10^{-9} mm. was obtained. The same one gram of potassium was used as in the previous tests, it was merely

redistributed in the trap by heating with a flame for a minute or two.

Discussion.

Extrapolation of the mercury-vapour pressure curve down to the temperature of liquid air would yield a value of the order 10^{-15} mm., an immeasurably small value. Yet when a liquid-air trap was used between the second ionization gauge and the pump, there was an apparent mercury-vapour pressure of 143×10^{-9} mm. This is certainly not due to mercury, so that in all probability it is due to the insufficient outgassing of the apparatus. The point of this investigation then is that, given the same degree of outgassing of the apparatus, fully as low a pressure can be obtained with a potassium trap as with a liquid-air trap. From the results with the first ionization gauge we may conclude that, with a potassium trap, the pressure of mercury vapour beyond it cannot exceed 5×10^{-9} mm., and may be many times less. We cannot of course say, without further investigation, that, with more strenuous outgassing, a potassium trap will be the equal of a liquid-air trap. Such a test would call for electronic bombardment of the anode and baking the gauge and connecting tubes in a suitable oven for a period of many hours or even days.

The spectroscopic experiments described at the beginning of the paper show that the power of potassium to act as a mercury-vapour barrier lasts for many weeks, in fact, until the potassium has taken up much more than its own weight of mercury. We did not carry out a similar test with an ionization gauge as that would have taken too long a time. One of us * used a sodium trap with an ionization gauge in a former research, and found that its effectiveness as a mercury-vapour barrier was very nearly as high at the end of a twenty-five day period as at any time before that.

The question arises as to whether the use of alkali metals might not be limited by the small but finite vapour pressure of the alkali metals themselves. Scott † has measured the vapour pressures of cæsium and rubidium, and from the empirical formulæ which he gives we may deduce that the vapour pressures at room temperature (say 300° K.) are respectively $5{\cdot}6 \times 10^{-6}$ and $2{\cdot}0 \times 10^{-7}$ mm. From these values one would not expect the vapour pressure of potassium at room temperatures to be much below 10^{-8} mm.

* F. E. Poindexter, Journ. Opt. Soc. America, ix, p. 629 (1924).
† D. H. Scott, Phil. Mag. xlvii. p. 32 (1924).

Yet the lowest value which we obtained for the pressure with the first ionization gauge was 5×10^{-9} mm. This is calculated on the assumption that the gas left is mercury vapour, since the gauge constants for other gases have not been determined and are not the same as that for mercury, though of course of the same order. We are inclined to believe that the values of the vapour pressures of the two alkali metals given by Scott are too high. Scott states that the pressure of mercury vapour passing a trap surrounded by CO_2 snow ($-50°$ C.) is as much as $1{\cdot}84\times10^{-4}$ mm. In an unpublished research by one of us (F. E. P.) on the vapour pressure of mercury at low temperatures, it was found that the pressure of mercury vapour passing a trap at $-50°$ C. was 2×10^{-7} mm., a value to be expected from the vapour-pressure curve. This is much smaller than Scott's value, and suggests some error in his method whereby his values are too high.

One of us (F. E. P.) is carrying out a systematic investigation of the vapour pressures of mercury-sodium and mercury-potassium amalgams as a function of the concentration of the mercury.

We have been informed by Mr. P. Lowe of Queen's University, Kingston, Canada, that he has found it advantageous to substitute sodium traps in place of liquid air traps in an investigation which he has completed on intensities in the hydrogen spectrum. In this investigation, which is probably typical of many, mercury lines in the spectrum could not be made to disappear until several days after liquid air had been placed around the traps, if the mercury vapour had once had access to the electrodes and the part of the apparatus where the spectrum was produced. To avoid this it was necessary to keep the traps continuously in liquid air, a rather costly procedure with a research lasting some months. Mr. Lowe found that about one gram of sodium in each trap acted as a satisfactory mercury-vapour barrier for the three months necessary to complete his observations.

Note on Technique.

As the main interest of this investigation is its practical application, it will not be out of place to offer a few remarks on the technique.

Any alkali metal may be used. Theoretical considerations lead us to expect that the trapping action would be most efficient with that metal having the highest heat of dilution

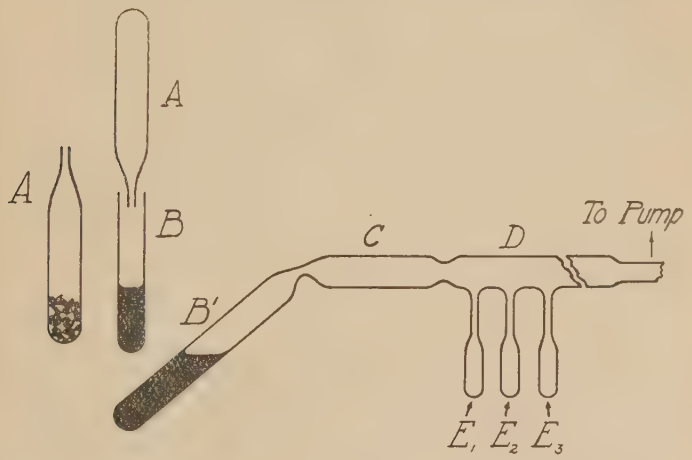
with mercury. Actually, however, we are limited in choice to sodium and potassium as the other alkali metals are rare and very expensive. As to sodium and potassium, sodium has the advantage in cost. but since we have found that a very small quantity of potassium retains its activity unimpaired for many weeks, the extra cost of the potassium is not a serious consideration. Sodium has also the advantage that its own vapour pressure is less than that of potassium. We have shown in this paper, however, that even with potassium a pressure of the order of 5×10^{-9} mm. can be obtained, and this is probably due to insufficient outgassing rather than to the potassium. Consequently it is only in the unexplored region of pressures below 10^{-9} mm. that the vapour pressures of the metals may possibly become a deciding factor in choosing between them. We are inclined to believe the vapour pressures of both metals at room temperatures are considerably below 10^{-10} mm. On account of the rapid change of vapour pressures with temperature, cooling the trap with ice would reduce the vapour pressure of the metal by a factor in the neighbourhood of ten as compared with its value at room temperature. This is regarded as a needless refinement, and it is not suggested as at all necessary in using the sodium or potassium as mercury-vapour traps. Potassium has the advantage that, owing to its lower melting and boiling points, it is decidedly easier to handle in pyrex glass apparatus.

We have developed a technique in preparing the sodium or potassium which may be helpful to others who may want to use one of these metals as a mercury vapour trap. The oil in which the sodium or potassium is supplied commercially occasionally contains a constituent which, if the metal is insufficiently washed with pure benzol or some such solvent, may be introduced into the vacuum system along with the metal, and may give a great deal of trouble in preventing the attainment of very high vacua. We have occasionally had to discard a complete system of pump, McLeod gauge, trap, and ionization gauge because of the accidental admission with the metal of this unknown substance, probably a hydrocarbon of high boiling-point. Consequently, we have developed a satisfactory method of cleaning and outgassing a large quantity of sodium or potassium and storing it in small glass tubes.

The technique of preparation is shown in fig. 4. A quantity of the metal amounting to four ounces or more is introduced straight from the bottles in which it was

purchased into a pyrex glass tube, about 3 to 4 cm. wide as shown in A. The upper part is drawn down to a width of about 5 mm. Then the metal is heated by a bunsen flame. As the heating is gradually increased the volatile hydrocarbons come off first and burn at the opening, then the heavier hydrocarbons. The heating is slowly increased until the metal itself begins to evaporate and condenses a little higher up the tube. At this stage, when all volatile impurities have been driven off, the tube is allowed to cool, but before the liquid begins to solidify it is poured into another pyrex glass tube B and allowed to solidify at the bottom. Most of the oxide etc. is left behind in A. B is then sealed on to a pumping system in

Fig. 4.



the position B′. The tube D has fused to it a dozen or more thin-walled glass tubes about 2 cm. long and 1 cm. in diameter and with necks of 4 mm. internal diameter. (These are the tubes in which the cleaned metal is ultimately stored.) When a vacuum has been obtained, the lower part of B′ is heated for a long time. The metal evaporates, condenses on the upper part of the tube B′ and runs down again, the action being that of a reflux condenser. At first large quantities of gas are evolved, but after several hours heating very little comes off. Then by heating the whole of B′ the metal is driven into C, and B′ is sealed off. Next the metal is liquefied in C, and by tilting the apparatus to the right (a flexible connexion between the apparatus and the pump allowed this) the metal flows

to D and fills all the small tubes E_1, E_2, etc. as it passes over them. These tubes are then sealed off in turn. In this way one can in two days or so prepare a sufficient stock of clean outgassed sodium or potassium which will be ample for several vacuum systems, as ordinarily used, for more than a year. The procedure is not so complicated as it seems, and is far preferable to inserting a piece of new potassium which has not been outgassed and which may carry a trace of heavy oil in with it enough to give trouble in the apparatus. Fig. 3 illustrates the way in which these small tubes are used. When the apparatus is assembled, a small tube E holding the potassium is opened and inserted into B, which is then sealed up at the open end. As soon as a good vacuum is obtained, the metal is liquefied by heat and runs down into A.

The shape of the tube on the inside of which the metal is finally distilled may be of many forms. Perhaps the right-angled joint in fig. 2 is as easy to make and as satisfactory as any.

If at any time one suspects that the metal is not acting as well as it should, redistribution of the metal by heating one part and then another of the trap for a minute or two will be found efficacious. It is our experience that this is seldom necessary, even when the surface of the metal is quite dull.

Summary.

(1) A liquid-air trap is almost universally used as a means for preventing mercury vapour diffusing back into a vacuum system from a mercury pump. It has been found that a trap lined with distilled alkali metal is as satisfactory a barrier to the passage of mercury vapour as a liquid-air trap. Any alkali metal may be used. Considerations of cost, however, practically limit one to either sodium or potassium.

(2) In this paper, we give a detailed investigation of the power of potassium (distilled so as to form a lining inside the trap) to stop mercury vapour passing back into the space to be exhausted. An ionization gauge was used to measure the residual pressure of mercury vapour. Using liquid air alone to trap the mercury vapour, the residual pressure in the ionization gauge after outgassing it by heat was $1{\cdot}4 \times 10^{-7}$ mm. The residual pressure, obtained on substituting a potassium-lined trap for the liquid-air trap, after precisely the same heat treatment, was $\cdot 74 \times 10^{-7}$ mm. These values are not regarded as residual

mercury-vapour pressures, they indicate that gases are being slowly evolved owing to insufficient outgassing of the apparatus. The lowest residual pressure obtained with a potassium trap after a more thorough outgassing of the ionization gauge and connecting tubes was 5×10^{-9} mm. It is probable that even this value is to be attributed to insufficient outgassing of the apparatus rather than to a genuine residual mercury-vapour pressure. In any case, we can regard it as the upper limit to the vapour pressure of mercury in a vacuum system beyond a potassium-lined trap.

(3) Several litres of moderately dry air may be passed over the potassium surface, making its surface a dull black without appreciably affecting its trapping power for mercury.

(4) Using the first appearance of mercury lines in the spectrum of helium at a pressure below ·01 mm. as a criterion, it has been found that a potassium-lined trap will act as a barrier to mercury vapour until the potassium has absorbed at least 150 per cent. of its own weight of mercury.

Washington University,
Saint Louis, U.S.A.,
May 17, 1925.

XLIII. *Note on a Method of Comparing Inductance and Capacity.* *By* T. B. Vinycomb, *M.C., M.A., Physics Department, Woolwich Polytechnic* *.

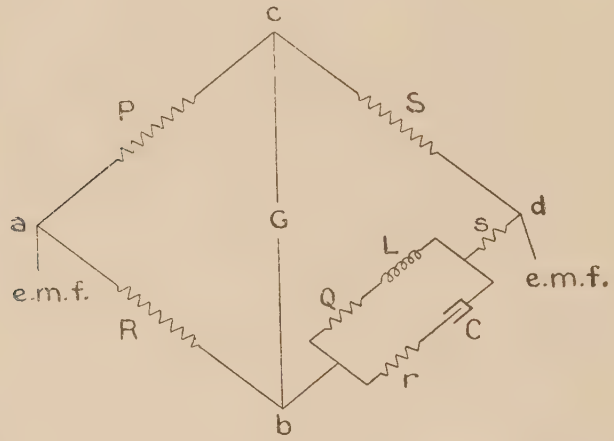
In the January number of the Philosophical Magazine, Professor Ganguli gives his experience in the use of the method proposed by Professor Forsythe in the 'Physical Review' of June 1913 for the comparison of a Self Inductance and a Capacity. He begins by quoting Professor Forsythe's theory. While the deduction is formally correct, the method of proof conceals to some extent the principle of the measurement.

On referring to the diagram in Professor Ganguli's paper, reprinted below, it is seen that a Wheatstone Bridge network is used, three arms of which are formed by non-inductive resistances, and the fourth arm is composed of a self inductance L and a capacity C, connected in parallel, each

* Communicated by the Author.

in series with a separate resistance. Another resistance is placed in the arm in series with both, as in the figure.

It is clear that a balance cannot be obtained under these conditions with alternating current, unless this arm is non-reactive, *i. e.* behaves as a pure resistance. The use of the bridge network, in fact, is merely for the purpose of determining when this condition is fulfilled. Any other method can be used by which it is possible to decide when the power factor of the arm is unity.



Let the impedance of this arm, neglecting s for the moment, be Z.

Then

$$\frac{1}{Z}=\frac{1}{Q+jpL}+\frac{1}{r+\frac{1}{jpC}}$$

$$=\frac{(Q+r)+j\left(pL-\frac{1}{pC}\right)}{\left(Qr+\frac{L}{C}\right)+j\left(pLr-\frac{Q}{pC}\right)}.$$

This will be equivalent to a resistance alone, if

$$\frac{Q+r}{Qr+\frac{L}{C}}=\frac{pL-\frac{1}{pC}}{pLr-\frac{Q}{pC}}, \quad \ldots\ldots \quad (1)$$

and this condition will be independent of p if

$$Q=r. \quad \ldots\ldots \quad (2)$$

Equation (1) leads to

$$LCp^2 = \frac{Q^2 - \frac{L}{C}}{r^2 - \frac{L}{C}},$$

so that for any values of Q and r, both greater or both less than $\sqrt{\frac{L}{C}}$, the arm is non-reactive for a particular value of p. This value becomes indeterminate if

$$Q^2 = r^2 = \frac{L}{C}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

as can also be seen by inserting (2) in (1) above.

Then $$Z = Q,$$

and the impedance for all frequencies is equal to the direct current resistance of the arm. The value of Q includes the resistance of the inductance L. There is no need to "swamp" this resistance as suggested by Professor Ganguli. When the condition

$$Q^2 = r^2 = \frac{L}{C}$$

holds, there is no need for the resistance s in the arm except to obtain a balance on the bridge. It is otherwise a disadvantage, as it reduces the sensitiveness. It should therefore be omitted, and the balance obtained by varying S. The balance does not depend on using equal ratio arms P and R, and any ratio may be used which is found convenient. If equal arms are used, it is easy to maintain the D.C. balance by making equal changes in Q and S. It may be noticed that the resistance required for A.C. balance is that which makes the circuit L, C, Q, r just aperiodic.

I have used this method for the measurement of Inductances between ·15 and ·0005 henry by comparison with a standard subdivided $\frac{1}{3}$ microfarad, and also to measure capacities down to ·002 microfarad against calibrated inductances, with satisfactory results when the value of Q did not exceed a few hundred ohms. When Q was 1000 ohms or over inaccuracy is likely to arise from two causes. First, self capacity of the resistances used will cause their values to depend on the frequency. In consequence, unless a pure sine-wave e.m.f. is used on the bridge, silence is not obtained

at balance, but merely a minimum of sound which is undefined except for a change in the faint note. Second, the setting for silence is more sensitive to an error in the adjustment for D.C. balance than to an error in the adjustment for A.C. balance when Q is large. This makes it difficult to compare two minima of sound separated by the interval of time required to change to new values of S, Q, and r. It is therefore preferable to arrange that the silence is searched for by adjustments of a different nature, not interfering with the D.C. balance. Of these there are two, a continuously variable L of constant resistance and a variable condenser. In any case, values should be chosen so as to make the resistances Q and r of moderate value to minimize these two difficulties and to increase the sensitiveness of the method. The sensitiveness cannot be safely increased by increasing the voltage applied to the bridge beyond a moderate value.

When approaching a balance the conditions can be best studied by considering the origin of out-of-balance current in the telephone. In both branches of the arm the current is out of phase with the voltage V between the ends. The leading component of the current in the capacity branch is equal and opposite to the lagging component current in the inductance branch when the bridge is balanced, and the difference of these two gives rise to the note heard. The currents in the two branches in phase with V combine to give no current in the telephone at balance.

The total current in the arm is $\frac{V}{Z}$.

$$\frac{V}{Z} = V\left(\frac{1}{Q+jpL} + \frac{1}{r+\frac{1}{jpC}}\right)$$

$$= V\left(\frac{Q-jpL}{Q^2+p^2L^2} + \frac{r+j\frac{1}{pC}}{r^2+\frac{1}{p^2C^2}}\right).$$

The current in the arm, in quadrature with V, is

$$I_1 = Vp\left(\frac{C}{p^2C^2r^2+1} - \frac{L}{Q^2+p^2L^2}\right)$$

$$= Vp\left\{\frac{CQ^2-L+Lcp^2(L-Cr^2)}{(1+p^2C^2r^2)(Q^2+p^2L^2)}\right\}.$$

This vanishes if $L = CQ^2 = Cr^2$.

These two conditions are not equally important, as can be seen by inserting numerical values.

Let $n=830$, i. e. $p=5000$ approx.; $L=10^{-2}$ henry; $C=10^{-7}$ farad. Then $Q=r$ should be $10^{5/2}$. $LCp^2=2{\cdot}5 \times 10^{-2}$, so that an error in $L-Cr^2$ may be 40 times as great as an error in CQ^2-L for equal effects in the telephones. The only term in the denominator of any importance is Q^2, so that on approaching balance the current which is in quadrature with V is

$$I_1=Vp\left(C-\frac{L}{Q^2}\right).$$

The component of the current in phase with V when near balance is

$$I_2=\frac{V}{Q}.$$

If Q_0 is the value of the resistance required for exact balance for both A.C. and D.C., and Q_0+dQ is the value used, the values of I_1 and ΔI_2 are

$$I_1=2Vp\frac{L}{Q_0^3}dQ,$$

$$\Delta I_2=-\frac{V}{Q_0^2}dQ,$$

and their effects in producing sound in the telephone will be proportional to these quantities. That is, they will be in the ratio

$$\frac{I_1}{\Delta I_2}=\frac{2pL}{Q_0}=2\tan\phi,$$

where ϕ is the angle of lag of the current in the inductance branch. It is therefore important for sensitiveness to keep $\frac{pL}{Q}$ large.

It follows that for ordinary values of the quantities concerned :—

1. The value of r is not critical, and may be left for final adjustment.
2. The method is not sensitive for small values of $\frac{C}{L}$, which require Q to be large.
3. The D.C. balance must be adjusted as accurately as possible if a good silence is to be obtained with A.C., *e. g.* by a slide wire in the arm S.

Taking these points into consideration, I have found that it is not difficult to obtain results concordant to less than $\frac{1}{4}$ per cent. and in agreement with measurements made by other methods. The accuracy of the comparison is improved by the use of non-reactive resistances and by eliminating earth capacity effects.

March 5th, 1925.

XLIV. *The Passage of an Alternating Current through Sulphuric Acid.* *By* R. T. Lattey, *B.Sc., M.A., The Electrical Laboratory, Oxford*.*

WHEN an E.M.F. is applied to platinum electrodes in acid solution the products of electrolysis cause a back E.M.F., and if the applied E.M.F. be removed the electrolytic cell will discharge itself, and is, in this way, analogous to a condenser. This analogy was recognized by Varley in 1860 (1), and was more fully investigated by Kohlrausch in 1869 (2). Various attempts were made to find the "capacity" of such a condenser (1, 3, 4, 5, 6, 7) by measuring the quantity of electricity given out after a cell had been charged to a measured voltage. It was Blondlot (7) who first pointed out that, since a cell of this kind gradually loses its E.M.F. on open circuit, it is analogous to a condenser short-circuited by a fairly high resistance.

If, following Kohlrausch, we regard the back E.M.F. as being proportional to the concentration (x) of one of the products of electrolysis, then

$$v = kx; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

and if the substance whose concentration is x is removed by diffusion or chemical action at a rate proportional to its concentration, then, while the cell is being charged by a current of strength i,

$$\frac{dx}{dt} = Ai - Bx, \quad \text{where A and B are constants.} \quad . \quad \text{(ii.)}$$

On open circuit we should have

$$\frac{dx}{dt} = \frac{1}{k}\frac{dv}{dt} = -Bx.$$

Whence $x = x_0 e^{-Bt}$ and $v = v_0 e^{-Bt}$.

According to Reichinstein (8) this law holds good, but

* Communicated by the Author.

his observations cannot be considered as very conclusive. It is interesting, however, to note the analogy of this law to the law $v = v_0 e^{-t/KR}$ when a condenser of capacity K is discharging through a resistance R.

Now suppose an alternating E.M.F. whose value at time t is given by $v = E \sin pt$ is applied to such a cell. Combining the equation $E \sin pt = kx$ with equation (ii.), we find that when a steady state has been reached the current "leads" on the voltage by an angle ϕ whose tangent is equal to p/B. A condenser of capacity K short-circuited by a resistance R would give a current leading by $\tan^{-1} pKR$; again we see the analogy between KR and B^{-1}.

In an actual cell we have, however, the resistance of the electrolyte between the plates (r), and there is also the possibility of a resistance (S) in the surface layers of the electrodes. The complete equations then become

$$\tan\phi = \frac{pKR^2}{R + (r+S)(1+p^2K^2R^2)} \text{ or } \frac{pkA}{(r+S)(p^2+B^2)+kAB},$$

$$\frac{E}{I}\sin\phi = \frac{pKR^2}{1+p^2K^2R^2} \text{ or } \frac{pKA}{p^2+B^2} \quad \text{(let us call this } 1/pC\text{)};$$

$$\frac{E}{I}\cos\phi = r + S + \frac{R}{1+p^2K^2R^2} \text{ or } r + S + \frac{kAB}{p^2+B^2}$$

(let us call this ρ).

Statements in the literature as to the connexion between p, pC, and $\rho - r$ are very conflicting

Observer.	Reference.	Periodicity.	Law.
Oberbeck	9	480–770	C = constant
Gordon	10	(30–60)10^3	C = constant.
Schönherr	11	530–1700	C = constant.
Warburg & Strasser	12	.....	$C\sqrt{p}$ = constant.
Krüger	13	390–3100	$C\sqrt{p}$ = constant.
Reichinstein	14	280–640	$C\sqrt{p}$ = constant.
Merritt	15	10^4–6×10^6	$C\sqrt{p}$ = constant.
Joliffe	16	6×10^5–10^7	$C\sqrt{p}$ = constant.
Sun.....	17	63–440	$C\sqrt{p}$ = constant.
Wien	18	400–1600	$C = M + Np^{-1}$.
Taylor & Curtis ...	19	1500–18,000	$C = M + Np^{-1}$ and $pC(\rho - r)$ = constant.
Haworth	20	620–1630	$C = M + Np^{-n}$ and $pC(\rho - r)$ = constant.
Wien	21	400–1600	$pC(\rho - r)$ = constant.

Haworth's n is a fraction which approaches unity for platinized electrodes; Krüger (13) found that C was constant for electrodes which had been feebly polarized by use as cathodes with direct current but that $C\sqrt{p}$ was constant for more strongly-polarized electrodes.

Comparatively few investigators have attempted to evaluate S and R; those who have done so agree that R must be regarded as infinite (or $B=0$); while Wien (21), Haworth (20), Joliffe (16), and Taylor and Curtis (19) have found that pCS is constant.

To some extent these discrepancies may be due to the fact that with some electrodes C and S are functions of the current strength; but in many cases the applied E.M.F. was not truly sinusoidal, *e.g.* Reichinstein (14).

The majority of investigators have used comparatively high periodicities, and it seemed to be of interest to try the effect of comparatively low periodicities.

Four pairs of electrodes were used, all of which had the same dimensions—circular disks of 2 cm. radius,—and in every case the electrolyte was H_2SO_4 . Aq. of maximum conductivity.

1st pair.—These were blackened by electrolysis, using a solution of chloroplatinic acid free from lead.

2nd pair.—These were first coated with platinum black by D.C. electrolysis with Lummer-Kurlbaum solution, and then heated until their surfaces were a dull mottled grey. They presumably contained a trace of lead.

3rd pair.—These were blackened like the second pair and used in a black condition.

4th pair.—These were used as received from the makers; their bright surface became dulled by use, and they acquired a dark brown surface layer which was easily removed by handling.

For the low frequencies employed a telephone was not a suitable detector when using a bridge method for measuring capacity and resistance; moreover, the only bridge method applicable to the case in hand is de Sauty's, and as this is independent of frequency, it does not afford any test of the presence or absence of harmonics in the E.M.F. wave. It was thought better to use a method which admitted the possibility of applying tests of the truly sinusoidal nature of the E.M.F. and current in the cell. Some observations were made with the well-known Joubert's wheel, and others with a rectifying commutator mounted on the same shaft as the armature of the dynamo. A commutator of this type gives average values of the current over a period corresponding to

half a wave, and does not therefore include any terms due to even harmonics.

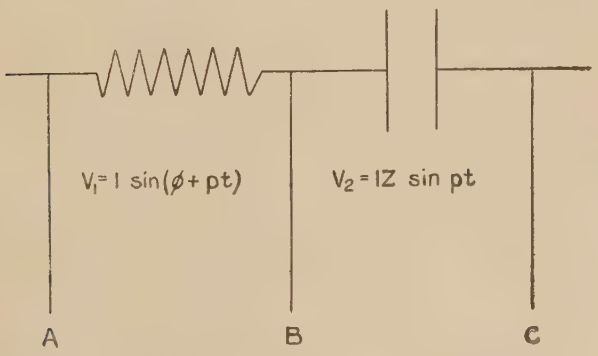
$$\frac{p}{\pi}\int_{\alpha}^{\alpha+\pi/p}\sin npt = \frac{p}{\pi}\left[-\frac{\cos npt}{np}\right] = \frac{1}{\pi n}\left[\cos\alpha - \cos(\alpha+n\pi)\right]$$

$$= \frac{2\cos\alpha}{\pi n} \quad \text{or } 0 \text{ according as } n \text{ is odd or even.}$$

The odd harmonics are seldom present to any appreciable extent in the voltage given by a dynamo, and hence the readings given by a rectifying commutator and galvanometer will correspond to the fundamental frequency only. Tests were made, however, and no evidence of the presence of odd harmonics could be obtained.

The position of the brushes of the commutator could be altered so that α had any desired value, and hence the complete voltage/time curve could be traced for any two points in the circuit to which they were connected. By connecting to the ends of a non-inductive 1-ohm coil (AB, fig. 1), the current/time curve could be traced. By

Fig. 1.



connecting with the terminals of the cell (BC, fig. 1) the voltage curve for this could be traced. This was done occasionally to ensure that E and I were truly sinusoidal; but the majority of the measurements were made as follows:— Galvanometer connected to AB, and commutator adjusted so that the galvanometer gave a zero reading; hence $\alpha_1 = \pi/2 = \phi + pt$; without altering the commutator, change the connexions to BC; then voltage indicated by galvanometer equals

$$\frac{2IZ}{\pi}\cos pt = \frac{2IZ}{\pi}\sin\phi = E_1.$$

Similarly, by adjusting so that the galvanometer reads zero when connected to BC and then switching over to AB, we

have $\alpha_2=\pi/2=pt$ and

$$\frac{2I}{\pi}\cos(\phi+\pi/2)=-\frac{2I}{\pi}\sin\phi=-E_2.$$

Set the commutator at $(\alpha_1-\pi/2)$, maintaining connexion to AB ; the reading now corresponds to

$$\frac{2I}{\pi}\cos 0^\circ=\frac{2I}{\pi}={}_mE_2.$$

By connecting to BC and setting the commutator at $(\alpha_2-\pi/2)$, we get $-{}_mE_1=\dfrac{2IZ}{\pi}$.

Readings were always taken for two pairs of values of α_1 and α_2 differing by 180°, so that galvanometer readings on opposite sides of the zero were obtained.

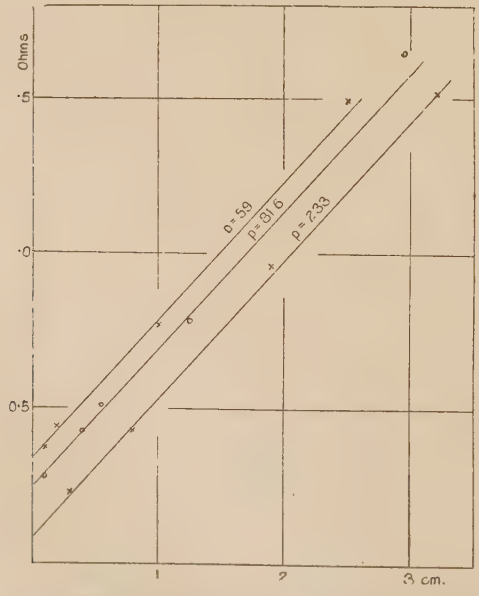
Then $\dfrac{E_1}{E_2}=\dfrac{{}_mE_1}{{}_mE_2}=Z$ and $\dfrac{E_1}{{}_mE_1}=\dfrac{E_2}{{}_mE_2}=\sin\phi$.

Hence $Z\sin\phi\,(=1/pC)$ and $Z\cos\phi\,(=\rho)$ could be calculated.

Results.

1. *Electrodes coated with pure Platinum.*—These were mounted in a tube only slightly larger in diameter than the

Fig. 2.

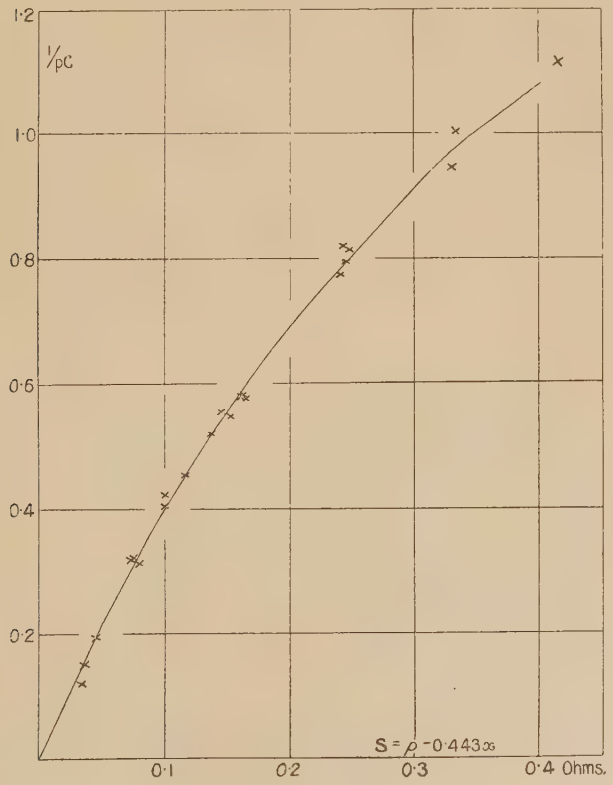


electrodes. In this way "edge-correction" for the resistance and capacity should be negligible. By varying the distance

between the electrodes and keeping other factors constant, it was found that ρ was a linear function of the distance (x) between the electrodes (see fig. 2), so that we can put $\rho = kx + S$, where k is constant—in this case equal to 0·443 ohm per cm.

S is clearly a function of p such that it increases when p diminishes. In what follows, $0{\cdot}443x$ has been subtracted from all observed values of ρ in order to obtain S.

Fig. 3.



Since it is not always easy to maintain the speed of the dynamo constant, it is better in the first instance to compare pC with S. By plotting $(p\mathrm{C})^{-1}$ against S (fig. 3), it is clear that a straight line does not represent the facts as it should if Wien, Haworth, or Taylor and Curtis are to be followed.

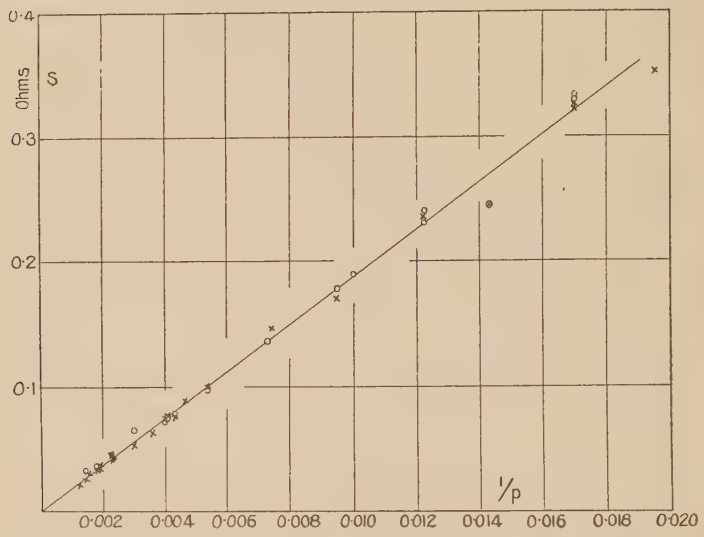
The curve drawn in fig. 3 was calculated by the equation

$$S(Bp\mathrm{C} - 1) = A, \text{ where } A = 0{\cdot}51 \text{ and } B = 2{\cdot}45 \quad \text{(iii.)}$$

With large periodicities—*i. e.* when pC is large—this will approximate to $p\mathrm{CS}=\mathrm{A}/\mathrm{B}=$ a constant, which will account for the statements of the authors quoted above, since they all used periodicities greater than 400.

In fig 4 values of S obtained directly are indicated by

Fig. 4.



circles, and those calculated from pC by the use of equation (iii.) by crosses. It will be seen that they indicate that

$$p\mathrm{S}=\mathrm{D}, \text{ where } \mathrm{D}=19{\cdot}2. \quad . \quad . \quad . \quad . \quad \text{(iv.)}$$

Combining this with equation (iii.), we have

$$p\mathrm{C}=(p\mathrm{A}+\mathrm{D})/\mathrm{DB}=(p+38)/92, \quad . \quad . \quad \text{(v.)}$$

which is in agreement with Wien, Taylor and Curtis, and Haworth.

2. *Grey Electrodes.*—These electrodes seemed to change their properties while an alternating current was passing, and it was very difficult to decide during a series of observations whether a steady state had been reached. The capacity seemed to depend on the strength of the current—a phenomenon observed by others in similar cases (22, 12, 23, 17, 18, 10). So far as any consistent results could be obtained, they appear to agree with a formula $308p\mathrm{C}=p+75+\mathrm{FI}$, where F is a constant and I equals current strength.

3. *Electrodes blackened with addition of Lead.*—These were set up in a large tank of acid with a distance of about 9 cm. between the electrodes. The resistance rose considerably

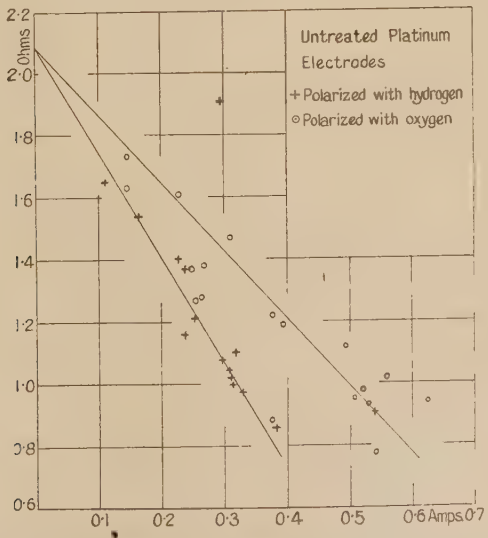
when the current was increased in strength and diminished with increase of periodicity as the following table shows :—

	I=0·14.	0·39.	0·53.
p=49·5	...	0·564	...
56·7	0·526	0·562	...
80·2	0·509	...	0·527
99·8	0·495	0·505	...
127	0·449	...	0·470
252	0·440	0·438	...
555	...	0·417	...

With currents below 0·1 amp. the effect of this factor was small compared with that of change of periodicity. But the electrodes underwent changes with time, and though, in a given series, values of ρ could be obtained which agreed with a formula $\rho = r + D/p$, the constant D changed from 7·5 to 43·5 and later to 14·25.

The capacity also changed, so that although in a given experiment $pC = A + pB$, the constants A and B changed from day to day.

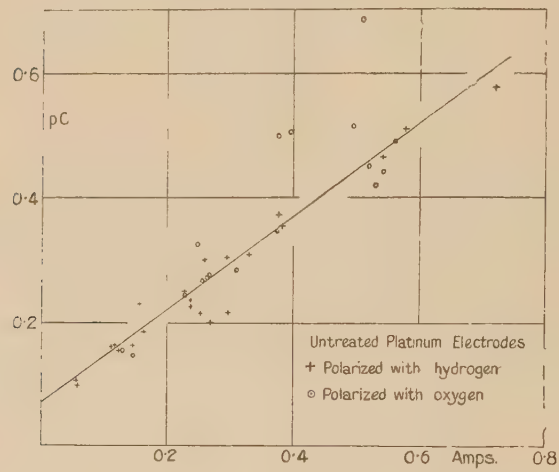
Fig. 5.



4. *Untreated Electrodes*.—These gave comparatively enormous values for $(pC)^{-1}$ and for ρ, and were exceedingly erratic in behaviour. They showed one unusual feature in that the resistence fell with increase in current strength (see fig. 5). Keeping the periodicity constant at 237 and

varying the current, it was clear that pC was a linear function of the current strength (see fig. 6); the experimental variations were much greater than the graph suggests, since we are here dealing with reciprocals: *e. g.*, the point

Fig. 6.



plotted as $p\mathrm{C}=0{\cdot}5$ at about 0·4 amp. corresponds to an observed value of 2, whereas from the graph $(p\mathrm{C})^{-1}$ should be $(0{\cdot}37)^{-1}$ or 2·7.

Summary.

The relationships between capacity (C), resistance (S), current strength, and periodicity (p) during the passage of an alternating current through H_2SO_4. Aq. have been investigated for values of p between 25 and 500 for four pairs of platinum electrodes.

	Effect of Increase of Current.		Effect of Increase of Periodicity.	
	(*a*) Capacity.	(*b*) Resistance.	(*a*) Capacity.	(*b*) Resistance.
1st pair ...	Negligible.	Negligible.	Decrease.	Decrease.
2nd pair ...	Increase.	*	Decrease.	*
3rd pair ...	*	Increase.	Decrease.	Decrease.
4th pair ...	Increase.	Decrease.	Decrease.	*

* Results too erratic to allow conclusions to be drawn.

The law connecting capacity and periodicity seems to be $pC = A + pB$, and that connecting resistance with periodicity $pS = D$, where A, B, and D are constants depending on the nature and condition of the electrode surfaces.

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XLV. *On the Stress-Optical Coefficients for Direct Tension and Pressure measured in the case of Glass.* *By* S. R. Savur, *M.A., University College, London* *.

1. *Historical.*

ONE of the fundamental assumptions made in the development of the theory of double refraction artificially produced in transparent media by mechanical stresses is that the optical effects of dilatation and compression are opposite, and that they are numerically equal when the stresses are equal. In spite of the importance of this assumption, it is

* Communicated by Prof. L. N. G. Filon, M.A., D.Sc., F.R.S.

surprising that very few accurate experiments seem to have been made hitherto to verify it.

Brewster (1), who was the first to direct attention to the subject of artificial double refraction, did very little quantitative work on the subject. This is probably due to the fact that accurate methods of measuring double refraction were of a later origin. He was, however, the first to use the method of observing simultaneously the effects of pressure and tension by putting a rectangular beam of glass under flexure. For reasons mentioned below, it will be seen that this method is not entirely satisfactory.

Neumann (2) contented himself mainly with the mathematical development of the theory of this subject. His conclusions were adversely criticised by subsequent experimenters, notably by Kerr (3) and Pockels (4), the latter of whom pointed out serious errors of calculation in Neumann's work.

Wertheim (12) seems to have been the first to put a block of glass and other materials under pure tension and pure pressure. The magnitude of the tensions used by Wertheim was severely limited, as it was applied by cementing hangers to a glass block, and naturally could not exceed the breaking strength of the cement. He states that this tension was as high as 50 kgm. wt./cm.^{2}, but an examination of his results shows that in many cases he did not go beyond a tension of 40 bars, and that in half the number of experiments the tension did not exceed 35 bars *.

One important conclusion he deduced from his experiments is the following. The double refraction is proportional to the mechanical extension or shortening, but is not strictly proportional to the stress producing it. On plotting the double refraction or the relative retardation of the two rays against stress as abscissa, he obtained, in the case of pressure, a curve which was concave towards the axis of stress, and in the case of tension a curve which was convex towards the same axis when the stresses were small; but as the stress increased these two curves were found to approximate to a straight line which was identical in the two cases.

The next prominent name that occurs in connexion with this subject is that of Kerr (3). He also put a plate of glass under direct tension (applied by friction grips), but used only two tensions, of which the greater only amounted to

* In one isolated case, that of "Verre à glaces," his results appear to indicate that he had applied a tension as high as 80 bars (*l. c.* p. 186), but it seems difficult to admit that any cement could have withstood a tension of this magnitude.

approximately 29 bars. On the whole, Kerr and most other experimenters have relied largely on flexure for obtaining information as regards glass under *tension*.

Two important objections may be raised against the flexure method. In the first place, in the case of a rectangular glass beam under flexure, the tension varies from point to point, and a small error in noting the position of a point on the plate will lead to a relatively large error in the calculated value of the stress-optical coefficient. A second, and more important, objection is the following. In experiments under flexure it is always presupposed that the stress varies linearly from the bottom to the top face, vanishing at the "neutral axis." This law is strictly true only in the case of perfectly elastic material; for any other material, the strain, but not necessarily the stress, follows a linear law. Moreover, if there be any permanent plastic flow, the readjustment of the material may seriously affect the stress and strain distribution, and it is known that glass shows plasticity under pressure (5).

None of the subsequent workers in this field seem to have verified this fundamental assumption, namely, that the optical effects of dilatation and compression are equal and opposite when the stresses are equal. Most of their conclusions are derived from observations of one type of stress only.

2. *Materials experimented on.*

The experiments described below were undertaken at the suggestion of Prof. Filon to test the accuracy of the law that the stress-optical coefficient is strictly the same for tension and for pressure, and particularly to see whether any deviation from the linear law, such as Wertheim suspected for small loads, actually exists. It was important to use the same specimen in both cases, as experience has shown that specimens nominally identical can differ widely in their stress-optical properties, and that even in one and the same specimen these properties can be affected by lapse of time (6). The difficulty of using the same piece of glass both for tension and for pressure lies, however, in the fact that whereas a long thin plate of glass is required for tension, a short thick one is most suitable in the case of pressure.

The plates of glass experimented upon were all supplied by Messrs. Adam Hilger & Co., with the exception of No. 1809 and U.V. 3492 originally supplied by Schott of Jena in 1906, and were of dimensions $13 \times 3 \times 1$ cm.^{3} The compositions of the glasses which are known are given in

Table I. Only one of them (1809) showed an initial double refraction, such as would be due to a pressure parallel to the

TABLE I.

	SiO_2.	PbO.	K_2O.	Na_2O.	Al_2O_3.	CaO.	B_2O_3.	MgO.
E.D.F. 4840	30·4	64·4	1·65	1·85	0·2	1·8	—	—
H.F. 6652	41·0	51·3	3·8	1·4	0·7	0·7	—	—
1809	35·4	18·7	7·4	—	3·7	—	34·3	0·5

longest edge of the plate. The remaining four seemed free from initial double refraction : the initial relative retardation was certainly less than $0{\cdot}006\lambda$, which is the smallest retardation that could be definitely detected.

3. *Optical Arrangements.*

Parallel and plane polarized monochromatic light was passed through a uniformly stressed specimen of glass, and the relative retardation was measured with a Babinet compensator in the manner described by Filon and Jessop (7).

Three different sources of monochromatic light were used, namely, a sodium flame and the green (5461 Å.U.) and the violet (4358 Å.U.) lines of a mercury arc lamp, each of the two monochromatic radiations being isolated by means of a suitable filter. For the mercury arc a capillary mercury lamp as described by Vincent and Biggs (8) was constructed. The intensity of light from this lamp was quite sufficient, and the arc remained in action without readjustment sufficiently long to allow a large number of readings to be taken.

The light was made parallel by means of a collimator and then polarized by reflexion so that the beam was horizontal and its plane of polarization inclined at an angle of 45° to the vertical.

The compensator was of the Babinet type giving a range of relative retardation from $+\frac{3}{4}\lambda$ to $-\frac{3}{4}\lambda$ in sodium light for a linear shift of approximately 25 mm. The wedges could be moved vertically by means of a micrometer screw, and the middle of the dark band under observation was registered on a fixed cross-wire. When the violet light of the mercury arc was used it was found difficult to see the cross-wire when the band was on it, and in this case recourse was had to lateral illumination to make the wire visible.

The method of observation was as follows :—After a load

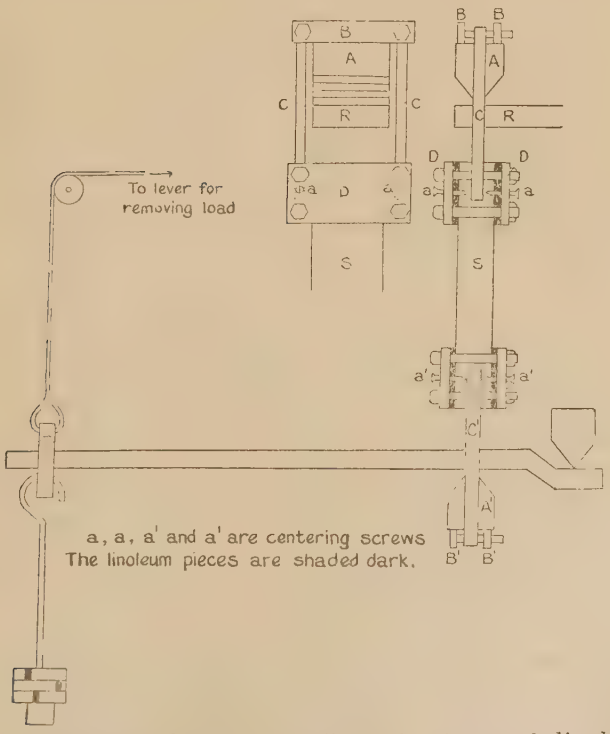
was put on, the analyser and the polarizer were crossed, and bands were seen corresponding to a relative retardation of an even number of half wave-lengths. The readings of the bands were taken, and the analyser then set parallel to the polarizer. This gave bands corresponding to a relative retardation of an odd number of half wave-lengths, giving another set of readings for the same stress and thus increasing the accuracy of the measurements. The error in a single reading was not more than about $0{\cdot}013\lambda$, and in general three readings were obtained for each load.

The optical arrangements were the same for both the pressure and the tension experiments.

4. *Apparatus for applying Direct Tension.*

The glass specimen S (fig. 1) was clamped tightly at each

Fig. 1.



end between two brass plates D with pieces of linoleum between the glass and the brass plates, so that a portion of the glass about 7 cm. long was left free in the middle. The

plates D were suspended by an arrangement of links, shown in fig. 1, from a knife-edge block A, a similar device being used at the other end.

The tension was applied by loading a lever X Y (fig. 1), which in turn applied a downward pressure to the knife-edge A′, the knife-edge A resting on a fixed support R. In order that the plane through the knife-edges A, A′ should pass accurately through the middle of the block, centering screws a, a, a', a' were provided, giving lateral adjustment. An arrangement of levers and pulleys enabled the load to be applied or removed without jar.

As the length of the glass left free between the clamps was about seven times its thickness, it was presumed that the end effects would not reach the middle of the specimen (9), and it was found on testing with the Babinet that the tension in the middle portion of the plate could be made quite uniform for a length of approximately 3 cm., the band remaining straight and horizontal.

The pieces of linoleum were found essential to (a) improve the grip and (b) grade the shear-stress at the edges of the grip, where otherwise a concentration of stress would inevitably have caused fracture under a moderate load.

The highest tension that could be applied without slipping occurring at the grips was roughly 92 bars, corresponding to a load of about 280 kilos. The tension was varied from 92 bars to 10 bars in nine equal steps.

5. *Apparatus for applying Pressure.*

The apparatus used for producing pressure was practically the same as that described by Filon (10). The pressure was applied to the specimen by means of two knife-edge blocks pressed together by a lever, the knife-edge blocks being adjustable for centering. As the glass plates were rather long, about 13 cm., a large pressure could not be applied lest the plates should buckle. The largest pressure used was, roughly, 102 bars and was well within Euler's limit for each of the plates.

One disadvantage of using the same plate of glass for both pressure and tension was that it was not practicable to employ with safety a stress more than about 100 bars; but the maximum tension reached is considerably more than that used by previous experimenters. This gave in a few cases a relative retardation as high as two wave-lengths, while the maximum relative retardation obtained by Wertheim in

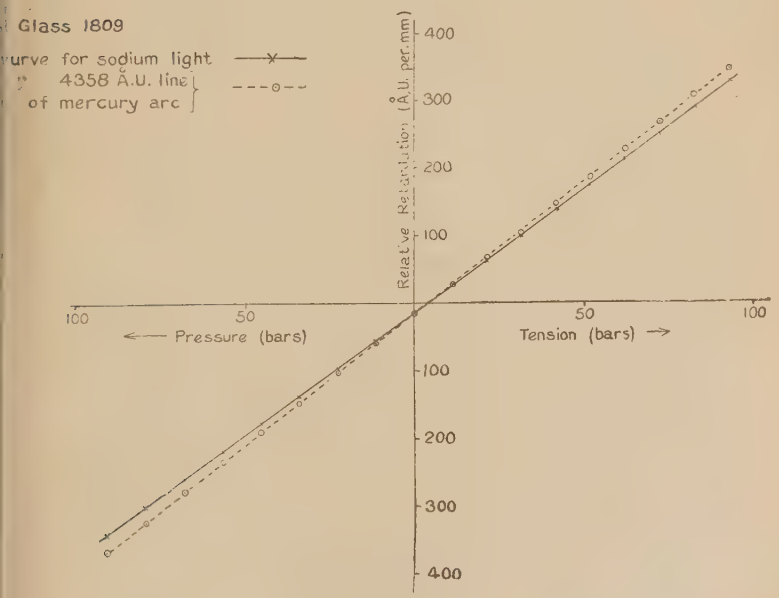
his tension experiments was, with one or two exceptions, only half a wave-length.

6. *Results obtained.*

It was observed that even under the maximum stress used the band took its final position simultaneously with the application of the load and that no residual effect could be observed when the load was completely removed, thus confirming the results (7) obtained by Filon and Jessop for glass.

The relation between the relative retardation for a given monochromatic light and the stress producing it was found to be linear in the case of the same substance, as the following diagram shows :—

Fig. 2.



The curves for the tension observations are the best fitting straight lines obtained by the method of least squares. Similar remarks apply to the pressure observations. The least square fit of a straight line for the tension and the pressure observations as a whole was also determined for each colour. It is not shown in the figure, as it would

practically coincide with the curves already drawn. The following table gives the results more fully :—

TABLE II.

Stress-Optical Coefficient in Brewsters *.

Glass.	λ 5893 Å.U.			λ 5461 Å.U.			λ 4358 Å.U.		
	T.	P.	T+P.	T.	P.	T+P.	T.	P.	T+P.
U.V. 3492.....	3·57	3·59	3·58	3·66	3·66	3·66	3·74	3·76	3·75
E.D.F. 4840 ...	1·39	1·38	1·38	1·38	1·38	1·38	1·24	1·24	1·24
H.F. 6652.....	2·29	2·29	2·29	2·29	2·30	2·30	2·30	2·31	2·30
B.S.C. 7641 ...	2·69	2·72	2·70	2·71	2·74	2·73	2·80	2·82	2·81
1809	3·64	3·59	3·62	3·77	3·74	3·75	3·89	3·85	3·87

* 1 brewster = a relative retardation of 1 Å.U. per mm. per bar.

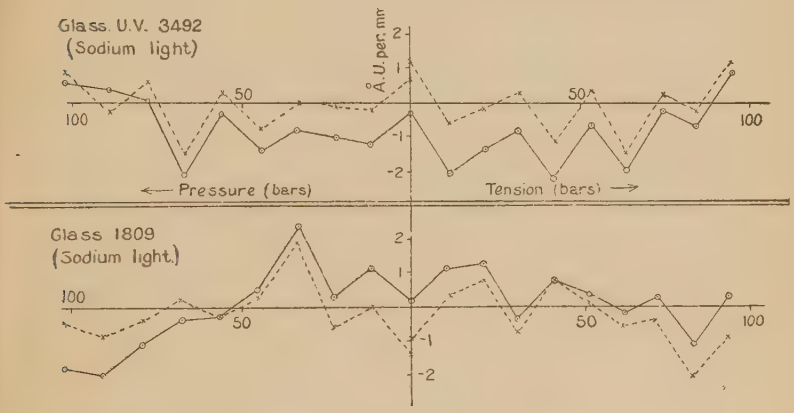
In each of the above cases the coefficient was determined from the best fitting straight line obtained from the method of least squares. T refers to tension only, P to pressure alone, and T + P to the two sets of observations taken as a whole.

It will be observed from the above table that though the individual stress-optical coefficients for tension and pressure, in the case of a given substance and monochromatic light, differ from each other by as much as 1·4 per cent. in one or two cases, yet they do not differ from the corresponding T + P coefficient by more than approximately 0·75 per cent., which is within the error estimated for the above measurements.

Fig. 3 shows the "residuals" from the straight line law in two typical cases. Two sets of residuals (calculated-observed) are shown in each diagram, the crosses indicating residuals from the best straight lines referring to tension and pressure separately, and the small circles residuals from the best straight line for both kinds of observations combined, the *sign* of the relative retardation being taken into account throughout. The upper diagram, which refers to U.V. 3592, shows the same general characteristics as the one for B.S.C. 7641, and the lower one refers to glass 1809. These two are selected as they exhibit the largest residuals.

In the upper diagram the residuals shown by small circles between +50 and −50 bars are all negative, while in the lower diagram they are all positive, with one exception. This is only to be expected, for in the former case the stress-optical coefficient for tension alone is less than that for pressure alone, while in the latter the reverse is the case.

Fig. 3.



It will be noticed that very few residuals exceed 2 Å.U. per mm., which is estimated to be the greatest error of the actual measurement. Although naturally a pair of straight lines can be adjusted to give a closer fit, in every case, than a single straight line, it is very difficult to be sure that the systematic divergences indicated by fig. 3 are really significant, and they might easily be due to some systematic error, such as an error in the initial reading, which might affect all pressure readings in one sense and all tension readings in the opposite sense.

We may conclude that, within the present limits of experimental error and up to a stress of 100 bars, the law connecting double refraction and stress is accurately linear and is the same for tension and for pressure.

There is no indication of any departure from this law for small loads, as suggested by Wertheim. In his paper (*l. c.* p. 186) he states that for a borosilicate crown glass containing zinc and potash, the pressure and tension loads for a retardation of $\frac{1}{2}\lambda$ were 151 kg. and 207 kg. respectively. This very considerable difference (about 30 per cent.) is in no way borne out by the present experiments, the borosilicate

(B.S.C. 7641) showing throughout very close agreement between the best straight lines for tension and pressure.

It seems probable that Wertheim's glass may have been imperfectly annealed: an unsuspected initial double refraction would easily account for a divergence of this kind. In the case of the present experiments, the existence of such initial double refraction was allowed for and is, in fact, indicated, where it exists, by the straight line, which fits the observations, not passing through the origin.

Nor does there appear to be any good ground for supposing that the double refraction is proportional to the strain, rather than to the stress. Wertheim's reason for suggesting this was that the general character of the strain-stress curve had certain resemblances to his retardation-stress curves. But, in view of the present observations, it seems probable that the departures of his retardation-stress curves from the linear law were due to errors of observation. The imperfect elasticity of glass is well known and, if the relation between retardation and *stress* is truly linear, it necessarily follows that the relation between retardation and strain cannot be linear.

7. *Some remarks on the Dispersion of Double Refraction in the glasses used.*

One interesting result of the experiments has been the discovery of a glass E.D.F. 4840 in which the stress-optical coefficient increases *numerically* from the violet *towards* the red.

A diagram given by Filon in 1903 (Camb. Phil. Proc. vol. xii. p. 335), showing the variation of both the stress-optical coefficient and the dispersion of double refraction in flint glass, with percentage of PbO, suggests that such a case could only occur for quite a small range of composition, between the percentage (about 66) corresponding to the vanishing of the dispersion and the percentage (about 75) corresponding to the vanishing of the stress-optical coefficient itself.

The results here obtained make $\frac{\Delta C}{\Delta \lambda}$ positive for E.D.F. 4840 (percentage of PbO, 64·4) and the dispersion sensibly nil for H.F. 6652 (percentage of PbO, 51·3). These values lie well outside the limits indicated by Filon's diagram, but it is to be noted that, whereas his dispersion is between the green and red, the dispersion here is between the indigo and yellow, so that the disagreement is probably only apparent.

Between 5461 and 5893, E.D.F. 4840 shows practically no dispersion, which suggests far better agreement.

It would seem that the dispersion (yellow-indigo) vanishes for a much lower percentage of PbO than 66—probably more like 55. Lead glasses showing such a pronounced dispersion of abnormal type do not appear to have been examined so far. Pockels found such an effect (but not very marked) in 0·500; it was, however, exhibited strongly in a *borosilicate* glass (0·428) examined by him. There is also an isolated observation by Macé de Lépinay (11), who gives, however, no details of his glass, so that it is not known whether it was a pure flint or borosilicate.

In conclusion the author wishes to express his obligations to Prof. L. N. G. Filon and to Mr. H. T. Jessop for their valuable suggestions and criticisms during the course of this investigation, which was carried out in the Applied Mathematics and Mechanics Laboratory at University College, London.

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XLVI. *Low-Voltage Arcs in Rubidium and Cæsium Vapours.*

By F. H. Newman, *D.Sc., A.R.C.S., Professor of Physics, University College of the South-West of England, Exeter* *.

1. *Introduction.*

In a previous paper † the author has discussed the investigation of low-voltage arcs in sodium and potassium vapours, and it was shown that the potentials required to strike and maintain arcs in these vapours depend primarily

* Communicated by the Author.
† Phil. Mag. xlix. p. 1057 (1925).

upon the vapour density and the temperature of the incandescent cathode, these potentials decreasing as the vapour density and the supply of electrons increase. The lowest striking potentials were obtained with intensely hot cathodes which, emitting a copious supply of electrons, provide conditions favourable for "photo-impact" ionization, and complete ionization of the vapour atoms is effected by electrons none of which have a velocity greater than that corresponding to the resonance potential of the vapour. In such cases the striking potential should equal the difference between the minimum ionizing and resonance potentials less the average emission energy of the electrons ejected from the cathode. Before ionization is attained the negative space charge limits the current to the value given by the well-known law $i = CE^{\frac{3}{2}}$ and also changes the uniform distribution of potential between the anode and the cathode. When this space charge is neutralized by positive ions, the arc strikes, giving a redistribution of electric intensity with a high potential fall in the immediate neighbourhood of the cathode. Under the influence of this comparatively large cathode fall an electron ionizes an atom at its first impact, and an arc can be maintained with a potential less than the ionizing potential, if the atoms are already in the metastable or partially ionized state. Before the negative space charge is annulled in this manner, some of the electrons emerge from the filament with an initial velocity which enables them to escape from the filament in spite of the negative potential gradient in the vicinity of the cathode, and the position of zero potential gradient is slightly removed from the cathode. As pointed out by Compton and Eckart * the fact that the electron current, which in low-voltage arcs is practically the entire current, flows against an opposing field is explained by the effect of diffusion arising from the large concentration gradient of the electrons. Usually this concentration gradient is negligible compared with the applied electric field, but with a high value it may become of primary importance, especially if the mean free path of the atoms is large.

These experimenters found that with abnormally low-voltage arcs in argon, operated at 6 volts, the cathode fall was invariably about 11·5 volts, which is the minimum radiating potential of argon. Under these conditions there was a reverse field of more than 5 volts existing throughout the greater part of the arc, and the electron concentration

* Phys. Rev. xxv. p. 139 (1925).

varied from the order of 10^{12} per c.c., just outside the cathode, to about 10^{10} per c.c. near the anode. They explain this reverse field by the difference in the mobilities of the electrons and the positive ions. In their experiments the gas potential, electron energy, and electron density all increased with increasing distance from the anode towards the cathode, and the voltage actually *increased* behind the cathode, attaining the maximum value of 11 volts 3 mm. away from the incandescent filament.

It has been found that some abnormally low-voltage arcs, notably those in helium and mercury, may be explained by the existence of electrical oscillations in which the peak voltage always exceeds the lowest radiating potential of the gas. Bär, v. Laue and Meyer *, and, independently, Compton and Eckart †, have shown that these oscillations are due to current interruptions produced by the rise in the current and consequent drop in the voltage which occur when the ionization is of sufficient intensity to create a positive space charge in the neighbourhood of the filament. Under these conditions the current increases to its saturation value, and the accompanying increased potential drop in the series resistances reduces the voltage across the arc to such a value that the atoms are no longer ionized. Until the previously excited atoms resume their normal state, the current through the arc falls, and the voltage rises, as the number of atoms in the metastable condition decreases, until the excitation of the atoms commences again and the cycle is then completed. The phenomenon resembles the singing arc between carbon electrodes, except that no inductance or capacity is necessary to maintain the oscillations in the abnormally low-voltage arc.

If E_i and E_r represent the ionization and resonance potentials, respectively, and if the atoms of the vapour are in the metastable condition, it is evident that the minimum striking potential should be $E_i - E_r - E_o$, where E_o is the energy with which the electrons are emitted from the incandescent filament and depends on its temperature. Thus with rubidium vapour, the ionization and resonance potentials of which are 4·16 and 1·59 volts respectively, the minimum striking potential should be $2{\cdot}57 - E_o$ volts, and in a similar manner, $2{\cdot}43 - E_o$ volts should be the minimum striking potential with cæsium vapour.

After the arc has struck, the condition within the discharge-tube changes in two essential aspects. The

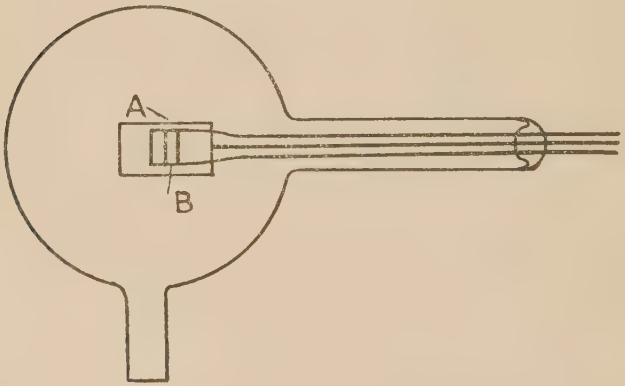
* *Zeit. f. Phys.* xx. p. 82 (1923).
† Phys. Rev. xxiv. p. 97 (1924).

negative space charge is neutralized by the positive ions, and the electronic emission from the filament is thereby greatly increased. Saturation may be approached or reached. In addition, a cathode fall is created by the accumulation of positive ions near the cathode, and this facilitates ionization of atoms which are already in an abnormal state. It is to be expected, therefore, that the arc may be maintained with a voltage less than that required to strike the arc, and the results obtained with rubidium and cæsium vapours, described below, confirm this.

2. *Experimental Arrangement.*

The arc tube, made of glass, fig. 1, was somewhat similar

Fig. 1.



in design to that used in the previous investigations. The anode A was of sheet metal about 3×5 cm. in size. The incandescent cathode B consisted of three tungsten wires arranged in parallel and giving a copious supply of electrons without necessitating an unduly large potential drop between the ends. The distance between these filaments and the anode was, approximately, 3 mm. To the bottom of the discharge bulb was fused a small tube containing the metal. The whole was exhausted, and the metal then distilled, under vacuum, into the bulb. Any gases liberated during this procedure were removed by the pump and the bulb, containing a quantity of metal sufficient to form a saturated vapour at the highest temperature used, was then sealed off from the rest of the apparatus. The bulb was enclosed within an electric furnace, the temperature of which could be maintained constant within 2 or 3 degrees.

The potential difference, obtained from a potentiometer arrangement, was regulated by a series of resistances, and was applied between the anode and the negative end of the filament, so that the voltmeter registered the maximum potential difference across the arc. In practice, the actual voltage across the filament was determined and the arcing potential difference was calculated from the centre of the filament. At low filament temperatures this method of measuring the effective voltage is probably correct, but at high temperatures it is probable that enough electrons leave the vicinity of the negative end of the filament to produce the arc, so that under these conditions the arc voltage should be measured between the anode and a point near the negative end of the filament.

3. *Experiments with Rubidium Vapour.*

With the filament current constant the striking potential was determined at different vapour pressures. The difficulty in this case was to determine the actual temperature between the electrodes since there must be a temperature gradient within the bulb owing to the heat from the filament. The latter tends to decrease the vapour density in the anode region, so that it was impossible to obtain more than an approximation of the temperature within the bulb.

It was found that above 180° C, the striking voltage and the potential necessary to maintain the arc both decreased, more or less uniformly, with increasing temperature. At each temperature the striking potential was observed several times until consecutive concordant results were obtained. One set of observations is shown in Table I. The voltages do not represent the true values; the latter being greater by the mean kinetic energy of the electrons, expressed in volts.

Table I.

Furnace Temperature.	Arc struck at	Arc maintained at
185° C.	7·3 volts.	7·0 volts.
200°	6·8	6·5
217°	5·9	5·5
233°	4·9	4·6
249°	4·0	3·7
265°	3·5	3·0
289°	3·2	2·3

The striking voltages with small filament currents were

high. This fact is explained by the total bombarding electron current producing insufficient ionization to cause an arc except at electron velocities well above the critical minimum velocity. Above a certain filament temperature both the striking and maintaining potentials decreased uniformly as the current through the filament increased, but the linear relationship did not hold at low filament temperatures. At the higher temperatures the supply of electrons and their average kinetic energy both increase, especially the electron current, so that the cumulative ionization effect becomes more prominent. With the vapour at 290° C. and the filament intensely bright, the arc could be struck at 2·9 volts and maintained at 2·1 volts.

The dependence of the striking and maintaining voltages on the filament current, the discharge bulb being at 290° C., is shown in Table II.

TABLE II.

Filament Current.	Arc struck at	Arc maintained at
12·6 amps.	3·3 volts.	2·4 volts.
11·8	3·8	2·9
10·2	4·3	3·4
9·6	4·8	4·2
8·8	5·5	5·0
8·2	6·2	5·8
7·8	7·3	6·8

Table III gives the data obtained when the discharge tube was at 185° C.

TABLE III.

Filament Current.	Arc struck at	Arc maintained at
13·1 amps.	6·9 volts.	6·2 volts.
12·4	7·1	6·4
11·2	7·6	6·8
10·3	8·2	7·5
9·4	8·8	8·3
8·8	9·4	9·0
8·2	10·3	10·0

In all experiments the establishment of the arc was immediately followed by a fall in the voltage across the electrodes, this drop in potential being brought about by the neutralization of the negative space charge. The appearance of a positive space charge in the neighbourhood of the

cathode facilitates an increased electron emission, and although the filament temperature remains constant, there will be a corresponding increase in the number of high-speed electrons emitted from the cathode. The maintenance of the arc under these conditions is due to the presence of atoms in the metastable state, the number of such atoms remaining constant. This type of ionization is important, not because of its contribution to the current, but because it facilitates the escape of additional electrons from the filament. It appears that the current through the discharge-tube must be carried in this case by the electrons, for if the positive ions were operative, their number would diminish with time and the arc would break. The electron current under these conditions is not, however, the normal electron emission which would be obtained with the heating current and applied voltage, since the positive space charge increases this normal electron current.

With rubidium vapour the chief factors which determine the production of low-voltage arcs are the high vapour density and the copious supply of electrons emitted from the incandescent cathode. Photo-impact ionization is, probably, particularly active in this case and accounts for the arc striking at potentials well below the ionization potential—4·16 volts—demanded by the quantum theory.

4. *Experiments with Cæsium Vapour.*

A discharge-tube similar to that shown in fig. 1 was used for the experiments with cæsium vapour, and the results obtained resembled those given by rubidium. In all cases ionization was observed below the ionization potential when the vapour density and electron densities were high. Under these conditions more electron-atomic collisions occur, more radiation is emitted and more is absorbed. The ionization and resonance potentials of cæsium vapour are 3·88 and 1·45 volts respectively, so that it should be possible, therefore, to strike the arc with an applied potential of $2{\cdot}43-E_o$ volts, where E_o represents the kinetic energy of the emitted electrons.

With the tungsten filament intensely bright and the vapour at 285° C., the arc could be struck readily at 2·6 volts and maintained at 1·9 volts. As the temperature of the discharge bulb was lowered these voltages increased in the way shown in Table IV. This is to be expected since a lower vapour density means fewer electron-atomic collisions and less radiation emitted.

Table IV.

Temperature of Furnace.	Arc struck at	Arc maintained at
164° C.	6·9 volts.	6·5 volts.
183°	5·8	5·4
201°	5·2	4·6
234°	4·1	3·4
252°	3·7	2·9
276°	3·1	2·3
295°	2·8	2·0

Table V. gives the striking and maintenance potentials with different filament currents, the temperature of the electric heater being 281° C.

Table V.

Filament Current.	Arc struck at	Arc maintained at
13·9 amps.	2·7 volts.	2·0 volts.
12·6	3·4	2·5
11·9	4·0	2·9
10·9	5·0	3·9
10·2	5·9	5·0
9·3	7·3	6·6
8·5	8·9	8·6

5. *Conclusions.*

It is evident that in cases where cumulative ionization is predominant low-voltage arcs may be maintained in vapours at voltages considerably lower than their ionization potentials. Atoms in the metastable condition are then ionized by direct impact, and the negative space charge around the incandescent filament is neutralized. As a result the supply of electrons is no longer entirely decided by the temperature of the filament, but there is in the immediate neighbourhood of the cathode an accelerating field which increases the electron current to its saturation value. It is possible to strike and maintain arcs in rubidium and cæsium vapours at potentials less than the ionization potential when the vapour density is high and when there is an intense electronic emission from the incandescent cathode.

XLVII. *A proposed Model for the Alpha Particle, and some Nuclear Series.* *By* R. Hargreaves *.

§ 1. THE present attempt to deal with some nuclear structures has a fundamental principle in common with an earlier paper † on Atomic Systems, but there is a substantial difference in the way the principle is applied. The principle is that atom or nucleus consists

* Communicated by the Author.

† Phil. Mag. December 1922.

of separate unit electrons—positive and negative. The paper combined these in one neutral structure; here they are separated into two groups, and we are now concerned with the inner group or nucleus.

Aston's theory of isotopes, in conjunction with the theory of spectral lines, suggests the assumptions which are made the basis of these structures.

(*a*) The atomic *weight* p, as narrowed by the use of a single isotope, is the number of positive electrons contained in the nucleus.

(*b*) The atomic *number* q is the number of negative electrons moving as satellites in orbits external to the nucleus, and controlled by the positive residue of the nucleus.

The difference $p-q$ is the number of negative electrons engaged in binding together the positive units so as to form a structure. The nucleus is taken to be a structure in the sense that all units contained revolve about a common axis, with their relative positions unaltered, under attractions and repulsions following electrostatic law. Further, it is supposed that nuclear orbits are on a much smaller scale than those of satellites.

It will follow that for the moderate range of the atomic number for which calculations are given, the reaction of satellites on elements of the nucleus will be small in comparison with the mutual action of the latter. It then becomes admissible to consider the nucleus independently of the external satellites: with large atomic numbers the assumption might be precarious.

Though an opinion that the nucleus is composite may be generally entertained, it is a somewhat hazardous adventure to put forward a definite structural scheme, even for a limited range of atomic numbers. The difficulties in making a structure conform to the requirements of atomic weights and numbers are serious enough, as the present attempt will illustrate. If these are overcome, there is I think an eventual test by reference to the spectral influences of the composite nucleus, the nature of which may be indicated. A composite nucleus gives a force only approximately that due to its positive residue acting at the centre. The departure from a normal potential energy has an effect on the orbits of satellites resembling that disclosed by Sommerfeld's treatment of a variable inertia, an effect due in each case to a second period involved. A comparison with observed spectra must

constitute a check on any proposed arrangement of the electrons within the nucleus.

§ 2. The scheme had its origin in the discovery of what seemed a reasonable model for the α particle. It differs from a model proposed by Lenz, and has the distinctive feature that the type can be extended into a series.

Now processes of disintegration natural or artificial point to a certain dominance of the helium type, which may be interpreted in two ways. It may be taken as demanding the assumption of a third fundamental entity in addition to the single positive and negative units, or as suggesting that the structure characteristic of the helium nucleus is one which admits of extension.

Further, the range of smaller atomic numbers comprises cases in which $p=2q$ as for helium, and others for which $p-2q=1$, the former suggesting a continuation of the type, the latter making a new call.

I now describe the primary series,—a triplane model.

In the upper and lower of three parallel equidistant planes equal circles are described by positive electrons, in the middle plane a circle of smaller radius is described by negative electrons, all circles having their centres on a common axis perpendicular to the planes. Each circle contains n elements equally spaced; positive lies over positive, but negative elements are in azimuth halfway between the positive. The circles are described with a common angular velocity.

Thus, for example, in the α model the four positive electrons lie at any moment at the four corners of a rectangle, the two negative at the ends of a perpendicular to the rectangle drawn through its middle point. The axis of rotation is a line through the middle of the rectangle drawn parallel to its shorter sides.

Attention may be called to two features of the model :— the position of the negative electrons in a plane between the planes of the positives, and on a circle of smaller radius, is one which gives strong protection to the more mobile electrons; the heavy positive electrons are placed where they contribute best to angular momentum.

§ 3. In virtue of the symmetry the dynamical equations are reduced to three, one securing the absence of an axial component of force on the positive elements, and two giving inertial forces in terms of attractions and repulsions for positive and for negative electrons. For helium ($n=2$) the inertial force on a negative electron has a less ratio than 1 : 3000 to that on a positive, and for higher values of n at any rate the ratio is less than 1 : 1840. If we are content with an accuracy of 1 in 1000, the inertial

force on a negative element may be neglected, that is such element must be very close to a position of equilibrium. We can then regard two of the equations as equations of condition determining the ratios of three distances, two radii and the perpendicular distance between planes; while the third gives the velocity of rotation.

Numerical solutions have been found for this primary series (i.) in the cases $n=2$, 3, and 4. In the two latter the solution is by trial, and the labour of course increases with the increasing number of attractions and repulsions. I have found it possible to obtain asymptotic formulæ for the sums of attractive and repulsive forces, based on the cosecant series considered in the former paper. The method gives simple results so long as only the terms of highest order are used, but the greater complexity of the present problem makes it laborious to deal with terms of less order.

It appears that the two equations described above as equations of condition can always be satisfied; but the third equation, which gives the value of ω^2 (ω=angular velocity), makes that value positive up to a certain value of n and thereafter negative. With only terms of highest order the value $n=18$ is indicated as final, but some examination of terms of lower order suggests an extension to $n=20$.

§ 4. Other series have been examined in which an addition is made to the primary form.

In series (ii.) the addition is that of a negative electron at the centre of the system. Solutions are found for $n=2$ and 3, main terms in the asymptotic value make ω^2 vanish for n between 23 and 24, and with terms of lower order $n=24$ is probably included.

In connexion with this series a new feature arises, viz. the question of stability of the central electron in respect to axial displacement. The position is unstable for small values of n, stable for higher values, with a place of transition only approximately determined (*cf.* § 7).

Where the series is applicable there are $2n$ positive and $n+1$ negative electrons within the nucleus, $(n-1)$ satellites; or if we call these $2q+2$, $q+2$, q, then $p=2q+2$. Thus with $n=23$ and 24 for the last two, these have $q=22$ and 23, $p=46$ and 48.

In series (iii.) the addition is that of two negative electrons on the axis at equal distances from the centre. A new variable is introduced with a corresponding condition for the equilibrium of the axial electrons, which greatly adds to the labour of numerical solution; and in fact only one has been found for the opening case $n=3$. The main term in the value of ω^2 is found to vanish for a value of n between 26

and 27, and the latter value is probably included when terms of lower order are taken into account.

The nucleus has $2n$ positive and $n+2$ negative electrons, and the number of satellites is $n-2$; or if these numbers are $2q+4$, $q+4$, q, then $p=2q+4$. The series opens with $q=1$, $p=6$, an isotope of hydrogen with mass 6 ; the last two have $n=26$, 27 or $q=24$, 25 and $p=52$, 54, and an intermediate case $n=20$ has $q=18$, $p=40$.

A modification of series (iii.) by the further addition of a positive electron at the centre has been examined and a numerical solution found for $n=3$. A difficulty arises in the application of the asymptotic method which I have interpreted as implying a very restricted series. The opening term with $n=3$, $q=2$, $p=7$ corresponds to an isotope of helium.

§ 5. It will be observed that the series (i.) terminates through lack of attracting power on the positive rings, a fact which points to the need for negative electrons in a higher ratio than 1 : 2 to the positive within the nucleus, to make a structure.

The only type which yields an odd number for isotope is the modified form of (iii.), a short series. In respect to odd values of atomic weights obtained otherwise than by a mixture of even isotopes, three types of addition to the primary series (i.) may be mentioned :—

(*a*) a pair near the centre,

(*b*) a central positive electron with two negatives revolving round it,

and (*c*) a central positive electron with three negatives revolving round it.

These additions give atomic weights and numbers corresponding to those in the series (i.), (ii.), and (iii.), but with a unit added to the weight. The configurations differ from the series types by always showing some departure from symmetry, and so there is left a problem of coordinating the added elements with the primary structure, which I have not faced.

A suggestion for dealing with higher atomic numbers will be made later, in which the proportion of negative to positive elements within the nucleus is gradually increased as the atomic number increases, where also odd and even isotopes stand on the same footing. *Cf.* § 16.

Numerical Solutions.

§ 6. It is proposed to write in detail the solution for the α particle, and to give a brief note of other numerical solutions. Take the radius of the circle described by the

negative electron as 1, that described by the positive electrons as a, and let $2b$ be the distance between the extreme planes. The three equations are then

$$\frac{1}{4}=\frac{4}{(1+a^2+b^2)^{3/2}},\quad \frac{1}{4b^2}+\frac{2b}{(4a^2+4b^2)^{3/2}}=\frac{2b}{(1+a^2+b^2)^{3/2}},$$

$$m_1\omega^2 a/\epsilon^2=-\frac{1}{4a^2}-\frac{2a}{(4a^2+4b^2)^{3/2}}+\frac{2a}{(1+a^2+b^2)^{3/2}}, \quad . \quad . \quad (1)$$

where in the first equation $m_2\omega^2/\epsilon^2$ is omitted, since m_2 and m_1 being masses of negative and positive electrons $m_2 : m_1 a$ is less than $1 : 3000$. The first equation yields $a^2+b^2=5{\cdot}3496$, the second is then $\frac{1}{b^3}=\frac{1}{2}-\frac{1}{(5{\cdot}3496)^{3/2}}={\cdot}41918$, and so $b=1{\cdot}3362$, $b^2=1{\cdot}7854$, $a^2=3{\cdot}5642$, $a=1{\cdot}8879$. The third equation gives $m_1\omega^2 a={\cdot}12795\epsilon^2$.

The kinetic energy is $(2m_1a^2+m_2)\omega^2$, and it is sufficient to write $K=2m_1a^2\omega^2$; the angular momentum is $(4m_1a^2+2m_2)\omega$, and it is sufficient to write $A=4m_1a^2\omega$.

In writing (1) and similar equations it is convenient to use ratios, but it is desirable to express the results in terms of r_1 the radius of the circle described by positive electrons. To pass from $m_1\omega^2 a={\cdot}12795\epsilon^2$, both sides are multiplied by a^2, then r_1 is written for a on the left hand and the numerical value of a^2 on the right hand. The solution may then be stated in the form

$$m_1\omega^2 r_1^3={\cdot}4560\epsilon^2,\quad K={\cdot}9121\epsilon^2/r_1,\quad A=4\epsilon\sqrt{m_1r_1}\times{\cdot}6753,$$
$$KA^2=4^2\epsilon^4 m_1\times{\cdot}4195. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For $n=3$ the equations are :

$$\left.\begin{aligned}&\frac{1}{\sqrt{3}}=\frac{2(2-a)}{(a^2-a+1+b^2)^{3/2}}+\frac{2(1+a)}{(1+a|^2+b^2)^{3/2}},\\&\frac{2b}{(a^2-a+1+b^2)^{3/2}}+\frac{b}{(a+1|^2+b^2)^{3/2}}=\frac{1}{4b^2}+\frac{4b}{(3a^2+4b^2)^{3/2}},\\&\text{and}\\&m_1\omega^2 a/\epsilon^2=-\frac{1}{a^2\sqrt{3}}-\frac{3a}{(3a^2+4b^2)^{3/2}}+\frac{1+a}{(1+a|^2+b^2)^{3/2}}\\&\qquad\qquad+\frac{2a-1}{(a^2-a+1+b^2)^{3/2}}.\end{aligned}\right\} \quad (3)$$

The solution is $a=1{\cdot}4684$, $b={\cdot}8112$, $m_1\omega^2 a={\cdot}25157$, and as referred to r_1

$$m_1\omega^2 r_1^3={\cdot}5752\epsilon^2,\quad K=1{\cdot}6273\epsilon^2/r_1,$$
$$A=6\epsilon^2\sqrt{m_1r_1}\times{\cdot}7365,\quad KA^2=6^2\epsilon^4 m_1\times{\cdot}8827.$$

For $n=4$, the solution is

$$a=1{\cdot}3013, \quad b={\cdot}5859, \quad m_1\omega^2 a={\cdot}3397,$$

and as referred to r_1

$$m_1\omega^2 r_1^3={\cdot}5752\epsilon^2, \qquad \mathrm{K}=2{\cdot}301\epsilon^2/r_1,$$
$$\mathrm{A}=8\epsilon^2\sqrt{m_1 r_1}\times{\cdot}7584, \quad \mathrm{KA}^2=8^2\epsilon^4 m_1\times 1{\cdot}3235. \qquad (4)$$

§ 7. Though the opening cases in series (ii.) are considered unstable, it may be well to state the solutions. For $n=2$ the equations (1) are modified to

$$1+\frac{1}{4}=\frac{4}{(1+a^2+b^2)^{3/2}},$$
$$\frac{1}{4b^2}+\frac{2b}{(4a^2+4b^2)^{3/2}}=\frac{2b}{(1+a^2+b^2)^{3/2}}+\frac{b}{(a^2+b^2)^{3/2}},$$

and

$$m_1\omega^2 a=\frac{a}{(a^2+b^2)^{3/2}}+\frac{2a}{(1+a^2+b^2)^{3/2}}-\frac{1}{4a^2}-\frac{2a}{(4a^2+4b^2)^{3/2}}; \qquad (5)$$

with a solution

$$a={\cdot}9072, \quad b={\cdot}5901, \quad m_1\omega^2\alpha={\cdot}8002\epsilon^2;$$

leading to

$$m_1\omega^2 r_1^3={\cdot}6585\epsilon^2.$$

For $n=3$, the solution is

$$a=1{\cdot}069, \quad b={\cdot}5481, \quad m_1\omega^2 a={\cdot}7603\epsilon^2;$$

leading to

$$m_1\omega^2 r_1^3={\cdot}8072\epsilon^2. \qquad (6)$$

The position as regards the axial stability of the central electron turns on the sign of the coefficient of z^2 in the expansion of

$$(1+z^2)^{-\frac{1}{2}}-(a^2+\overline{b-z}^2)^{-\frac{1}{2}}-(a^2+\overline{b+z}^2)^{-\frac{1}{2}},$$

where z is a small axial displacement of the electron. This coefficient is $-\frac{1}{2}+\frac{a^2-2b^2}{(a^2+b^2)^{5/2}}$; the first term only, due to the circle of negative electrons, would give instability, and accordingly stability demands a condition

$$2a^2-4b^2>(a^2+b^2)^{5/2}. \qquad (7)$$

If we write the sign of equality, and then differentiate with regard to a^2 to get a further equation $4=5(a^2+b^2)^{3/2}$, the combination gives values $a^2={\cdot}6894$, $b^2={\cdot}1723$. The position is then that no case of the inequality occurs if $b^2>{\cdot}1723$; but as b^2 is diminished there is a range of values

of a^2 above and below ·6894 for which the condition is satisfied, and this range is continually extended until when b approaches 0, the range of a is from 0 to $\sqrt[3]{2}$ or 1·26. Judging from the values of a, I estimate that the inequality first holds for $n=8$, which corresponds to $q=7$.

This discussion of stability has an application to the addition of a pair to the primary series suggested above (*cf.* § 5). For the opening terms the position, being unstable for a negative electron at the centre, is stable for a positive electron. The pair would therefore have its positive element very close to the centre, and a dynamical complication which would attach to the reverse arrangement is minimized. This addition of a pair would in the case of $n=3$ make $p=7$, $q=3$ an isotope of lithium.

§ 8. For type (iii.) a single case $n=3$ has been solved. With $+c$ and $-c$ for the axial positions of the added negative electrons, the equations are :

$$\left.\begin{aligned}
&\frac{1}{\sqrt{3}}+\frac{2}{(1+c^2)^{3/2}}=\frac{2(2-a)}{(a^2-a+1+b^2)^{3/2}}+\frac{2(1+a)}{(a+1|^2+b^2)^{3/2}},\\
&\frac{2b}{(a^2-a+1+b^2)^{3/2}}+\frac{b}{(a+1|^2+b^2)^{3,2}}+\frac{b-c}{(a^2+b-c|^2)^{3,2}}\\
&\qquad+\frac{b+c}{(a^2+b+c|^2)^{3/2}}=\frac{1}{4b^2}+\frac{4b}{(3a^2+4b^2)^{3/2}},\\
&\frac{3(b+c)}{(a^2+b+c|^2)^{3,2}}=\frac{3(b-c)}{(a^2+b-c|^2)^{3,2}}+\frac{3c}{(1+c^2)^{3,2}}+\frac{1}{4c^2},\\
&m_1\omega^2a/\epsilon^2=-\frac{1}{a^2\sqrt{3}}-\frac{3a}{(3a^2+4b^2)^{3/2}}+\frac{1+a}{(1+a|^2+b^2)^{3/2}}\\
&\qquad+\frac{2a-1}{(a^2-a+1+b^2)^{3/2}}+\frac{a}{(a^2+b+c|^2)^{3/2}}+\frac{a}{(a^2+b-c|^2)^{3/2}};
\end{aligned}\right\}\quad(8)$$

of which the solution gives

$$a=1\cdot126,\ b=\cdot707,\ c=1\cdot075,\ m_1\omega^2a=\cdot8844\epsilon^2,$$

leading to

$$m_1\omega^2r_1^3=1\cdot121\epsilon^2.$$

When the equations are modified to correspond with the addition of a positive electron at the centre, the solution obtained is :

$$\left.\begin{aligned}
&a=1\cdot803,\ b=\cdot987,\ c=1\cdot008,\ m_1\omega^2a/\epsilon_2^2=\cdot4245;\\
&\text{leading to}\qquad m_1\omega^2r_1^3=1\cdot381\epsilon^2.
\end{aligned}\right\}\quad(9)$$

§ 9. Application of Quantum.—The numerical solutions give the ratios of the three distances concerned in (i.) and (ii.), and of the four concerned in (iii.). The scale on which the system is constructed is so far arbitrary. After some hesitation I have set down values in which the system is made definite by equating the angular momentum of each positive electron to the standard angular momentum $h/2\pi$ of Planck's method. The combination of equations

$$m_1\omega r_1^2 = h/2\pi \quad \text{and} \quad m_1\omega^2 r_1^3 = \mathrm{N}\epsilon^2 \quad . \quad . \quad (10)$$

will then be found to yield the following results :—

$$r_1 = 2{\cdot}89\times10^{-12}\times\mathrm{N}^{-1}, \quad \mathrm{K} = m_1\mathrm{V}^2\times5{\cdot}29\times10^{-5}\times n\mathrm{N}^2,$$
$$v/\mathrm{V} = 7{\cdot}27\times10^{-3}\times\mathrm{N}\,; \quad . \quad . \quad . \quad . \quad (11)$$

where v/V is the ratio of linear velocity of a positive electron to that of light.

These numbers are based on the values of constants given by

$$h = 6{\cdot}565\times10^{-27}, \quad \epsilon = 4{\cdot}774\times10^{-10}, \quad \epsilon/m_2 = 5{\cdot}3\times10^{17},$$
$$m_1/m_2 = 1840. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

A table of some numerical values will be given when the asymptotic position has been dealt with. *Cf.* § 14.

§ 10. Asymptotic Values.—The general form of the equations for the primary series will be set down with a view to considering asymptotic values* when n is great. The fact that the inertial force on a negative electron is negligible is expressed by the equation

$$\frac{c_n}{2} = \sum_{r=0}^{r=n-1} \frac{2(1-a\cos\theta_r)}{(1+a^2+b^2-2a\cos\theta_r)^{3/2}}\,; \quad . \quad . \quad . \quad (\mathrm{A})$$

in which $\theta_r = (2r+1)\pi/n$, and c_n defined as $\frac{1}{2}\sum_{s=1}^{s=n-1}\operatorname{cosec} s\pi/n$ has the asymptotic value

$$c_n = \frac{n}{\pi}\left(\log_e n + \gamma - \log_e\frac{\pi}{2}\right). \qquad (13$$

The vanishing of the axial component of force on a positive electron is secured by an equation

$$\sum_{r=0}^{r=n-1} \frac{b}{(1+a^2+b^2-2a\cos\theta_r)^{3/2}} = \frac{1}{4b^2} + \sum_{s=1}^{s=n-1} \frac{2b}{(2a^2+4b^2-2a^2\cos\theta_s)^{3/2}}, \quad . \quad (\mathrm{B})$$

in which $\theta_s = 2s\pi/n$.

* For the analysis *cf. op. cit.*, section Mathematical Theory.

A third equation gives the value of ω^2, viz.

$$m_1\omega^2 a/e^2 = -\frac{c_n}{2a^2} - \sum_{s=1}^{s=n-1} \frac{a(1-\cos\theta_s)}{(2a^2+4b^2-2a^2\cos\theta_s)^{3/2}} + \sum_{r=0}^{r=n-1} \frac{a-\cos\theta_r}{(1+a^2+b^2-2a\cos\theta_r)^{3/2}}. \quad (C)$$

To deal with asymptotic values we require at the outset some conception of the probable order of the quantities. In the double ring of earlier work, x being a ratio of radii of circles in one plane, I found $(x-1)n^2$ to be a finite quantity, and with this in mind looked to some modification of the type $\alpha+\beta\log n$ for $(a-1)n^2$. The forecast is verified and permits a reduction of $1+a^2+b^2-2a\cos\theta_r$ to a form $b^2+2a(1-\cos\theta_r)$ or $b^2+4a\sin^2\theta_r/2$, and $2a^2+4b^2-2a^2\cos\theta_s$ to a form $4(b^2+a^2\sin^2\theta_s/2)$.

Further to make use of the binomial expansion we need some assurance of the relative values of b and $\sin\theta_r/2$. For this purpose a limiting case may be considered in which an infinite lattice-work is taken as model. In each of two infinite parallel lines positive units are placed at distance $2x$, positive opposite to positive, so that four adjacent units form a rectangle of sides $2x, 2y$. Negative units are placed at the centre of each rectangle. The condition of equilibrium in its original form is

$$\frac{1}{4y^2}+\frac{4y}{(4x^2+4y^2)^{3/2}}+\frac{4y}{(16x^2+4y^2)^{3/2}}+\frac{4y}{(36x^2+4y^2)^{3/2}}+\dots = \frac{2y}{(x^2+y^2)^{3/2}}+\frac{2y}{(9x^2+y^2)^{3/2}}+\frac{2y}{(25x^2+y^2)^{3/2}}+\dots,$$

or

$$\frac{1}{8y^3}+\frac{1}{4(x^2+y^2)^{3/2}}+\frac{1}{4(4x^2+y^2)^{3/2}}+\frac{1}{4(9x^2+y^2)^{3/2}}+\dots = \frac{1}{(x^2+y^2)^{3/2}}+\frac{1}{(9x^2+y^2)^{3/2}}+\frac{1}{(25x^2+y^2)^{3/2}}+\dots,$$

or with $y^2=\mu x^2$,

$$\frac{1}{2\mu^{3/2}}+\frac{1}{(2^2+\mu)^{3/2}}+\frac{1}{(4^2+\mu)^{3/2}}+\frac{1}{(6^2+\mu)^{3/2}}+\dots = 3\left[\frac{1}{(1+\mu)^{3/2}}+\frac{1}{(3^2+\mu)^{3/2}}+\frac{1}{(5^2+\mu)^{3/2}}+\dots\right]. \quad (14)$$

If $\mu<1$ expansion of each term by the binomial may be made, and with a notation

$$S_3=\frac{1}{1^3}+\frac{1}{2^3}+\frac{1}{3^3}+\ldots,\quad T_3=\frac{1}{1^3}+\frac{1}{3^3}+\frac{1}{5^3}+\ldots,$$

and use of the property $S_3/2^3=S_3-T_3$, the equation takes the form

$$\frac{1}{2\mu^{3/2}}+S_3-\frac{3}{2}\mu S_5+\frac{3}{2}\frac{.5}{.4}\mu^2S_7-\ldots$$

$$=4\left(T_3-\frac{3}{2}\mu T_5+\frac{3}{2}\frac{.5}{.4}\mu^2T_7-\ldots\right). \quad . \quad . \quad (15)$$

The solution $\mu=\cdot4308$ (*v. infra*) justifies the expansion, and in the circular problem where x is replaced by $a\pi/n$, we shall find that br proves finite, and b is less than the least value of $2\sin\theta_r/2$ or $2\sin\pi/2n$. Accordingly we may write

$$(1+a^2+b^2-2a\cos\theta_r)^{-3/2}$$

$$=\{2a(1-\cos\theta_r)+b^2\}^{-3/2}$$

$$=\frac{\operatorname{cosec}^3\theta_r/2}{8a^{3/2}}\left[1-\frac{3}{2}\cdot\frac{b^2}{2^2a}\operatorname{cosec}^2\theta_r/2\right.$$

$$\left.+\frac{3}{2}\frac{.5}{.4}\frac{b^4}{2^4a^2}\operatorname{cosec}^4\theta_r/2-\ldots\right],$$

or with Σ_3 for $\sum_{r=0}^{r=n-1}\operatorname{cosec}^3\theta_r/2$,

$$\sum_{r=0}^{r=n-1}(1+a^2+b^2-2a\cos\theta_r)^{-3/2}$$

$$=\frac{1}{8a^{3/2}}\left(\Sigma_3-\frac{3}{2}\cdot\frac{b^2}{2^2a}\Sigma_5+\frac{3}{2}\frac{.5}{.4}\frac{b^4}{2^4a^2}\Sigma_7\right). \quad . \quad (16)$$

If we write main terms only,

$$\Sigma_3=2T_3\times\left(\frac{2n}{\pi}\right)^3,\ \Sigma_5=2T_5\times\left(\frac{2n}{\pi}\right)^5, \quad . \quad . \quad . \quad (17)$$

and then the main term in $\sum_{r=0}^{r=n-1}(1+a^2+b^2-2a\cos\theta_r)^{-3/2}$ is

$$\frac{2n^3}{\pi^3a^{3/2}}\left(T_3-\frac{3}{2}\beta T_5+\frac{3}{2}\frac{.5}{.4}\beta^2T_7\ldots\right), \quad . \quad . \quad . \quad (18)$$

where β is used for $b^2n^2/a\pi^2$.

To deal with $\{2a^2(1-\cos\theta_s)+b^2\}^{-3/2}$ we need a formula $2S_3\times\left(\frac{n}{\pi}\right)^3$ for the main term of

$$\sum_{s=1}^{s=n-1}\operatorname{cosec}^3 s\pi/n, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and so obtain as main term of $\sum_{s=1}^{s=n-1}(2a^2+4b^2-2a^2\cos\theta_s)^{-3/2}$ the value

$$\frac{n^3}{4\pi^3a^3}\left(S_3-\frac{3}{2}\frac{\beta}{a}S_5+\frac{3\,.\,5}{2\,.\,4}\frac{\beta^2}{a^2}S_7\ldots\right). \quad . \quad . \quad . \quad (20)$$

The condition (B) is therefore expressed by

$$2(T_3-\tfrac{3}{2}\beta T_5+\ldots)=\frac{1}{4\beta^{3/2}}+\frac{1}{2a^{3/2}}\left(S_3-\frac{3}{2}\frac{\beta}{a}S_5+\ldots\right). \quad (21)$$

The asymptotic form in which a is written $=1$ is

$$2(T_3-\tfrac{3}{2}\beta T_5+\ldots)=\frac{1}{4\beta^{3/2}}+\tfrac{1}{2}(S_3-\tfrac{3}{2}\beta S_5+\ldots); \quad . \quad (22)$$

it agrees with (15) above, and depends not only on the use of $a=1$ but also on accepting as sufficient the main terms in the values of Σ_3....

§ 11. In dealing with (A) the numerator $1-a\cos\theta_r$ is written as $a(1-\cos\theta_r)-(a-1)$, and so long as only a main term is in question we treat a as 1 in the various expansions. In the series with $1-\cos\theta_r$ as numerator we have Σ_1 appearing which is $2(c_{2n}-c_n)$, and then (A) is represented by

$$\frac{c_n}{4}=\tfrac{1}{2}(c_{2n}-c_n)-\frac{n}{\pi}\left(\frac{3}{2}\beta T_3-\frac{3\,.\,5}{2\,.\,4}\beta^2T_5+\ldots\right)$$
$$-\frac{2n^3(a-1)}{\pi^3}(T_3-\tfrac{3}{2}\beta T_5+\ldots),$$

or by

$$\frac{2n^2(a-1)}{\pi^2}\left(T_3-\frac{3\beta}{2}T_5+\ldots\right)=\frac{1}{4}\left(\log_e n+\gamma+\log_e\frac{32}{\pi}\right)$$
$$-\left(\frac{3}{2}\beta T_3-\frac{3\,.\,5}{2\,.\,4}\beta^2T_5+\ldots\right). \quad . \quad (23)$$

when the value of c_n in (13) is introduced. This gives to $a-1$ the form stated above.

A convenient way of dealing with (C) is to take it in conjunction with (A), viz. add (C) to the result of dividing (A) by $2a$; which has the effect of giving to $(1+a^2+b^2-2a\cos\theta_r)^{3/2}$ a numerator $a+a^{-1}-2\cos\theta_r$, which to a

close approximation is $2(1-\cos\theta_r)$. Thus in lieu of (C) we have

$$m_1\omega^2 a/\epsilon^2+\frac{c_n}{4a}+\frac{c_n}{2a^2}=-\sum_{s=1}^{s=n-1}\frac{a(1-\cos\theta_s)}{(2a^2+4b^2-2a^2\cos\theta_s)^{3/2}}+\sum_{r=0}^{r=n-1}\frac{2(1-\cos\theta_r)}{(1+a^2+b^2-2a\cos\theta_r)^{3/2}}.$$

The results of previous summations now give when $a=1$ a value

$$m_1\omega^2/\epsilon^2=c_{2n}-\frac{9}{4}c_n+\frac{n}{2\pi}\left(\frac{3}{2}\beta S_3-\frac{3.5}{2.4}\beta^2 S_5+\ldots\right)-\frac{2n}{\pi}\left(\frac{3}{2}\beta T_3-\frac{3.5}{2.4}\beta^2 T_5+\ldots\right)$$

$$=\frac{n}{4\pi}\left[\log_e(128\pi)-\gamma-\log_e n+2(\tfrac{3}{2}\beta S_3-\&c.)-8(\tfrac{3}{2}\beta T_3-\&c.)\right]. \quad (24)$$

Thus it appears that when the numerical value of β is found, we have a given by (23), b by the definition of β as $b^2n^2/a\pi^2$, and ω by (24).

The solution of (22) proves to be less difficult than it appears. The numerical series denoted by S and T have values greater than 1 by amounts which converge rapidly as the suffix is increased, viz. with $S_3=1+S_3'$, ...

$$\left.\begin{array}{l} S_3'=\cdot20206,\ S_5'=\cdot03693,\ S_7'=\cdot00835,\ S_9'=\cdot00201,\\ \qquad\qquad S_{11}'=\cdot00049,\ \ldots\ldots\\ T_3'=\cdot05180,\ T_5'=\cdot00452,\ T_7'=\cdot00047,\ T_9'=\cdot00005,\ \ldots \end{array}\right\} \quad (25)$$

With $\beta<1$,

$$S_3-\tfrac{3}{2}\beta S_5+\ldots=\frac{1}{(1+\beta)^{3/2}}+S_3'-\tfrac{3}{2}\beta S_5'+\frac{3.5}{2.4}\beta^2 S_7'+\ldots,$$

and so (22) stands

$$\frac{6}{(1+\beta)^{3/2}}+8(T_3'-\tfrac{3}{2}\beta T_5'+\ldots)=\frac{1}{\beta^{3/2}}+2(S_3'-\tfrac{3}{2}\beta S_5'+\ldots). \quad (26)$$

If the residual series are neglected, $6^{2/3}\times\beta=1+\beta$ or $2\cdot302\beta=1$ or $\beta=\cdot4344$. The difference of the residues proves small, and a corrected value is $\beta=\cdot4308$. With

this, and again making use of $S_3 = 1 + S_3'$, we obtain

$$\left.\begin{aligned} S_3 - \frac{3}{2}\beta S_5 + \ldots &= \cdot 7651, & T_3 - \frac{3}{2}\beta T_5 + \ldots &= \cdot 6333, \\ \frac{3}{2}\beta S_3 - \frac{3.5}{2.4}\beta^2 S_5 + \ldots &= \cdot 5337, & \frac{3}{2}\beta T_3 - \frac{3.5}{2.4}\beta T_5 + \ldots &= \cdot 4477. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (28)$$

With these values, (23) becomes

$$\frac{2n^2(a-1)}{\pi^2} \times \cdot 6333 = \tfrac{1}{4}\log_e n + \cdot 2768,$$

or

$$n^2(a-1) = 1 \cdot 948 \log_e n + 2 \cdot 157, \quad . \quad (28)$$

and (24) is

$$m_1\omega^2/\epsilon^2 = \frac{n}{4\pi}(2 \cdot 9053 - \log_e n) = \mathrm{N} \text{ say.} \quad . \quad (29)$$

§ 12. The equations (23) and (24) may be corroborated by use of the equation $2K + P = 0$, connecting kinetic and potential energies. The attraction section of P which contributes the positive element to 2K, that is to $2nm_1\omega^2a^2$, has a term ϵ^2 multiplied by

$$2n \sum_{r=0}^{r=n-1} (1 + a^2 + b^2 - 2a\cos\theta_r)^{-\frac{1}{2}}, \text{ or } 2n \Sigma (4a \sin^2\theta_r/2 + b^2)^{-\frac{1}{2}},$$

or

$$\sum_{r=0}^{r=n-1} n\left[\operatorname{cosec}\theta_r/2 - \frac{1}{2}\left(\frac{b}{2}\right)^2 \operatorname{cosec}^3\theta_r/2 + \ldots\right],$$

which is

$$n\left[2(c_{2n} - c_n) - \frac{4n}{\pi}\left(\frac{\beta}{2}T_3 - \frac{1.3}{2.4}\beta^2 T_5 + \ldots\right)\right]. \quad . \quad (30\,a)$$

With the opposite sign is a repulsive term,

$$-n \sum_{s=1}^{s=n-1} (2a^2 + 4b^2 - 2a_1^2\cos\theta_s)^{-\frac{1}{2}},$$

or

$$-nc_n + \frac{n^2}{\pi}\left[\frac{1}{2}\beta S_3 - \frac{1.3}{2.4}\beta^2 S_5 + \ldots\right]; \quad . \quad . \quad (30\,b)$$

with which is associated

$$-n/2b \quad \text{or} \quad -n^2/2\pi\beta^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad (30\,c)$$

For the repulsive potentials of elements in the same circle there is division by 2 as well as multiplication by n, with a result

$$-\frac{nc_n}{2}\left(1 + \frac{2}{a}\right). \quad . \quad . \quad . \quad . \quad . \quad (30\,d)$$

Thus finally for $a=1$, we get

$$m_1\omega^2 = c_{2n} - \tfrac{9}{4}c_n - \frac{n}{4\pi\sqrt{\beta}} + \frac{n}{2\pi}\left(\frac{1}{2}\beta S_3 - \frac{1\cdot 3}{2\cdot 4}\beta^2 S_5 + \ldots\right) - \frac{2n}{\pi}\left(\frac{1}{2}\beta T_3 - \frac{1\cdot 3}{2\cdot 4}\beta^2 T_5 + \ldots\right). \quad (31)$$

If we subtract this from (24) we find a difference

$$\frac{n}{4\pi\sqrt{\beta}} + \frac{n\beta}{2\pi}(S_3 - \tfrac{3}{2}\beta S_5 + \ldots) - \frac{2n\beta}{\pi}(T_3 - \tfrac{3}{2}\beta T_5 + \ldots),$$

the vanishing of which constitutes the equation (22).

§ 13. The distinctive feature of the results is the appearance of a negative coefficient for the term $\log_e n$ in (29), which gives a termination to the series and at the same time leads to certain maxima and minima. We find, in fact:

(*a*) ω^2 vanishes for $\log_e n = 2{\cdot}9053$, that is for $n = 18{\cdot}3$.

(*b*) $\frac{dN}{dn} = 0$ for $\log_e n = 1{\cdot}9053$ or $n = 6{\cdot}72$, giving a maximum for N and, when the quantum condition is applied, a minimum for r_1.

(*c*) $\frac{d}{dn}(nN^2) = 0$ for $\log_e n = 2{\cdot}2386$ or $n = 9{\cdot}31$, giving a maximum value of K.

(*d*) $\frac{d}{dn}(nN) = 0$ for $\log_e n = 2{\cdot}4053$ or $n = 11{\cdot}1$, giving a minimum for the distance between the planes, as we proceed to explain.

If the quantity β defined by $n^2b^2/a\pi^2$ is to be treated as a pure number, then when distances $(r_2\, r_1\, z)$ replace $(1, a, b)$ we must suppose that $\beta\pi^2 = n^2b^2/a$ is replaced by

$$\beta\pi^2 = n^2z^2/r_1r_2, \quad \text{or} \quad z^2/r_1^2 = \beta\pi^2/an^2. \quad . \quad . \quad (32)$$

As $r_1^{-1} \propto N$, it is clear that $z^{-1} \propto nN$.

The magnitude of the shortest distance between elements is a matter of some importance in a nuclear system of this kind. Between positive elements that distance is $2z$, or when ratios only are concerned $2b$; and when n is great the distance between a positive and the nearest negative electron is approximately $\sqrt{b^2 + a^2\pi^2/n^2}$. Now

$$4b^2 : b^2 + a^2\pi^2/n^2 = 4\beta : \beta + a = 4\beta : \beta + 1$$
$$= 1{\cdot}7232 : 1{\cdot}4308 = 1{\cdot}204.$$

For higher values of n the distance between next adjacent

positive and negative elements is about 9 per cent. less than $2z$ the distance between extreme planes. For helium we have $4b^2 : 1+a^2+b^2 = 1{\cdot}124$, and the shortest distance is about 6 per cent. less than the distance between extreme planes. As this is a small variation, a value of $2z$ may be taken as giving a sufficient clue to the magnitude of the shortest distance between elements.

§ 14. The difficulty in constructing a table of values, say for the primary series, lies in the fact that an asymptotic formula cannot be expected to give good values for small numbers, and the independent numerical solutions extend only to $n=4$.

On comparing the values of a and b (the latter through the β connexion) given by the asymptotic formulæ with the solution for $n=4$, the value of a is less than ·2 per cent. in excess, that of b less than ·5 per cent. in excess, of values obtained by solution. These are conspicuously favourable results, but the formula gives values 16 per cent. in defect for the value of ω^2, largely due to writing $a=1$ in the formulæ of approach to (29). The weakness occurs in a vital point, since the coefficient in the value of ω^2 determines the scale of dimensions when the quantum method is applied.

Attention will be given to a partial correction for values of n near the conclusion of the primary series, for which ω^2 is small, and so any terms neglected become of special importance. If in the terms containing c^n we do not write $a=1$, we shall obtain

$$m_1\omega^2 a^3/\epsilon^2 = c_{2n}\sqrt{a} - c_n(1+\tfrac{1}{2}\sqrt{a})^2 + \text{series in } \beta :$$

it is proposed to examine the increment in the terms written. To the first order in $(a-1)$ they are :

$$c_{2n} - \tfrac{9}{4}c_n + \tfrac{1}{2}(c_{2n} - \tfrac{3}{2}c_n)(a-1)$$

or

$$c_{2n} - \tfrac{9}{4}c_n + \frac{n(a-1)}{4\pi}\left(\log\frac{32n}{\pi} + \gamma\right). \quad . \quad . \quad (33)$$

The first descending term in c_n is $\pi/72n$, which gives a correction $7\pi/144n$ to be applied to $c_{2n} - \frac{9}{4}c_n$. We also find for

$n=18$, $a-1=$·024, original N ·0213, addition to N ·2056, corrected N ·227
„ 19, „ ·022, „ −·0593, „ ·1971, „ ·138
„ 20, „ ·020, „ −·1438, „ ·1914, „ ·0476 } , . . . (34)

in which it has been presumed that series in β are less seriously affected.

We can now give a short table of initial and final terms for the primary series.

n.	a.	N.	r_1.	$2z$.	κ.
2	1·888	·4560	6·338	8·972	2·195
3	1·468	·5424	5·328	5·914	4·669
4	1·301	·5752	5·024	4·524	7·001
.....				.....	
18	1·024	·227	12·73	2·88	4·91
19	1·022	·138	20·94	4·44	1·91
20	1·020	·0476	60·7	12·40	·24

In this table

(1) a is the ratio of radii $r_1 : r_2$;

(2) the distances r_1 and $2z$ are the digits given with a factor 10^{-12};

(3) the kinetic energy $= m_1 V^2 \times 10^{-5} \times \kappa$, where κ is the number in the last column.

§ 15. It is proposed to state briefly the asymptotic position in reference to other series.

For (ii.) the right-hand member of (23) would contain an extra term $-\pi/2n$, and that of (22) an extra term $-\pi^2/n\sqrt{\beta}$, both of an order neglected in the work for (i.).

The alteration in ω^2 is on a higher scale, and is most readily found by the method of § 12.

The terms added to potential energy are $-2n\epsilon^2(a^2+b^2)^{-\frac{1}{2}} + n\epsilon^2$, and therefore the terms added to $m_1\omega^2 a^3/\epsilon^2$ or to $m_1\omega^2 r_1^3/\epsilon^2$, that is to N, have a value $a(a^2+b^2)^{-\frac{1}{2}} - a/2$, which approaches the limit $1/2$ when n is increased.

In series (iii.) there is a new variable c, with an equation

$$\frac{n(c+b)}{(a^2+c+b|^2)^{3/2}} + \frac{n(c-b)}{(a^2+c-b|^2)^{3/2}} = \frac{nc}{(1+c^2)^{3/2}} + \frac{1}{4c^2}, \qquad (35)$$

required to secure the equilibrium of axial negative electrons. With b/c assumed to be negligible and $a=1$ this equation is reduced to $nc(1+c^2)^{-3/2} = 1/4c^2$, or approximately $c^3 = 1/4n$, a value which makes b/c of order $n^{-2/3}$.

Again, in (B) we have extra terms $(b-c)(a^2+b-c^2)^{-3/2} + (b+c)(a^2+b+c^2)^{-3/2}$, in which the main contributions of the c terms are cancelled and $2b$ is an approximate value, small in comparison with the term $1/4b^2$. The alterations to b and a, the latter judged as above for (ii.), are then small.

The potential energy has extra terms $-2n\epsilon^2/\sqrt{a^2+c-b^2} - 2n\epsilon^2/\sqrt{a^2+c+b^2} + 2n/\sqrt{1+c^2} + \epsilon^2/2c$, contributing to the

value of $-2K$ or $-2nm_1\omega^2a^2$. Thus an approximate value of the terms added to N is $1/\sqrt{1+c^2}-1/4nc$, or $1-c^2/2-1/4nc$, or $1-3/8nc$, or $1-\frac{3}{8}\times\left(\frac{2}{n}\right)^{2/3}$.

Lastly, in series (iii.) as modified by a positive electron at the centre, the equation (35) is replaced by

$$\left.\begin{aligned}&\frac{1}{c^2}+\frac{n(c+b)}{(a^2+\overline{c+b}|^2)^{3/2}}+\frac{n(c-b)}{(a^2+\overline{c-b}|^2)^{3/2}}=\frac{1}{4c^2}+\frac{nc}{(1+c^2)^{3/2}},\\ &\text{or when } b/c \text{ is negligible,}\\ &\frac{3}{4nc^3}+\frac{2}{(a^2+c^2)^{3/2}}=\frac{1}{(1+c^2)^{3/2}}.\end{aligned}\right\}\quad(36)$$

This equation requires

$$(a^2+c^2)^{3/2}>2(1+c^2)^{3/2}\quad\text{or}\quad a^2-\sqrt[3]{4}>c^2(\sqrt[3]{4}-1),$$

that is $a^3>2$.

In the primary series, as n is increased a approaches 1 as limit; I have no doubt this is valid with any finite modification such as we are considering, and draw the conclusion that the series is of limited extent. In the primary series the value of a is already below the limit $a^3=2$ when $n=5$, but in this modification the position is more favourable, as giving $a=1{\cdot}803$ for $n=3$ while $a=1{\cdot}468$ in (i.).

The series is then probably confined to the cases $n=3$ to $n=5$, and its three examples have $p=7$, $q=2$; $p=9$, $q=3$; $p=11$, $q=4$.

§ 16. The three series cover only a moderate section of the whole range of atomic numbers.

The limitation in (i.) and the extensions provided in (ii.) and (iii.) point to the need of a stronger attracting force on the positive elements; or we may say that the demand is for a higher ratio of negative elements to positive than 1 : 2. We have reached the limit of negatives which can be added in special positions, and if the problem can be dealt with by addition to the main structure that addition must contain positive as well as negative elements. It is proposed to consider such an addition in the form of the double ring which was the subject of my earlier work, and to suppose it placed in the central plane inside the main structure. The proposal will be examined under two aspects—adaptation to given atomic weight and number, and capacity to provide attraction on the positive rings of the triplane.

If m is the number of positive or negative elements in the double ring, then $p=2n+m$ and in series (i.), (ii.), (iii.)

n has the respective values q, $q+1$, $q+2$. As example *, take the case of Ag where $q=47$, and Aston gives 107, 109 as ascertained values of p. The arrangement for $p=107$ shows $m=9$, $n=49$ in (iii.), $m=11$, $n=48$ in (ii.), $m=13$, $n=47$ in (i.). An increase of m by 2 is needed to pass to the case $p=109$. If a minimum value of m is taken, series (iii.) appears in both cases; and then isotopes have the same n, but are distinguished by the use of different values of m.

In the matter of providing attraction for the positive elements of the triplane, (iii.) should be more efficient than (ii.), and (ii.) than (i.), since a position of negative electrons on the axis or at the centre assists in giving an external position to the negative ring in the double ring (*v. infra*). Thus, for large values of n at any rate, (iii.) only is likely to appear and one combination corresponds to one isotope.

The central double ring may be expected to make its appearance on the completion of the original series, beginning with $m=2$ and gradually requiring higher values of m. The case $m=1$ I refer to the heading (α) of § 5, which is or may be operative from $n=3$ forwards within the range of the original series.

§ 17. We consider now in general terms the mutual action of the double ring and the triplane.

The double ring alone (*i. e.* under no external force) is a plane structure with positives in the outer circle, with radii tending to equality as m is increased, and with a value of $m_1\omega^2a^3/\epsilon^2$ approaching a limit $m\times\cdot441$ or $2m\pi^{-1}\log_e 2$.

For a combination of the two types occurring first as n approaches a value 30, the action of the triplane on interior electrons does not differ much from that of a single ring of n positive electrons in the central plane. It tends to draw the negative electrons of the double ring away from the centre and to push the positive towards the centre, an action which is aided in (ii.) and (iii.) by a central or two axial negatives. When the action is sufficient to place the circle of negative electrons in the external position, the double ring exercises an attraction on the positive elements of the triplane, depending specially on m and on the difference of radii which the external force (of the triplane) is capable of securing.

The demand for attraction on the positive elements of the

* The only values to which I have access are those in 'Nature,' Sept. 22nd, 1923.

triplane naturally increases as the number n increases. But whereas for small values of m a change in the ratio of radii is easy to bring about, it becomes increasingly difficult when m is greater and the relative closeness of elements gives to near neighbours a controlling influence on the ratio. Thus we should expect to find, as n is increased, a demand for a more than proportionate increase in m. We do, in fact, find that in the range $q=31$ to $q=47$, if a like choice of arrangements (in respect to series used) is made, m increases by 6 while n increases by 16; whereas later the increments become more equal, and finally that of m exceeds that of n or q.

Again, the action of the double ring on the two positive rings of the triplane tends to make the latter approach, and so to diminish the number β. This has the effect of increasing the number 2·905 in N, *cf.* (24) and (29), which was obtained by subtracting terms in the β section from $5{\cdot}42-\log_e n$. The amount subtracted would be diminished, and thus further aid given towards increasing the value of N.

These arguments are qualitative, and point to the action being in the sense requisite to make the scheme of completion feasible. Whether its intensity is adequate, only calculation can show: possibly the nature of the co-ordination of the two sections would be revealed in the course of adjustment of numerical values.

As with the primary series and its two extensions, so with this new addition it would appear probable that a terminus will be reached beyond which no construction of the type is valid.

§ 18. The existence of the atom in the shape of nucleus and satellites indicates a greater difficulty in incorporating negative electrons in the structure of the nucleus than in attaching them at relatively great distances; so that the former process is carried only so far as may be needed to overcome the mutual repulsion of positive elements. This feature is, I think, to be connected with the very different mean velocities of positive and negative electrons in a space where both are sparsely distributed. The accumulation of a positive residue in the nucleus tends to counteract this influence by providing an attraction for negative as against repulsion for positive electrons outside.

If we suppose that in such a space pairs are formed in a number of cases, then positive and negative free electrons are in the same position as regards attraction to a pair,

supposing them to pass near to one or other member of the pair. But in the case of the positive electron the average relative velocity is on a smaller scale than for the negative, and there is a longer period of contiguity in which the attraction is effective. The combination of two positives at the end of a diameter with a negative at the centre is therefore more probable than the contrary arrangement, and special prominence attaches to the triplet * (2+, 1−).

But further steps are more conjectural. The readier attachment of members having moderate or small relative velocity would, if pairs were fairly numerous, suggest the formation of a linear series of pairs (or linear series of alternate + and −), where a considerable approach to equilibrium of forces would be attainable except at the terminals, which might be supposed to swing round so as to form a closed circuit. In like manner from a formation resembling the lattice model of two positives to one negative, the same failure in adjustment near the terminals might lead to the closure of the circuit giving the triplane model. The process of completion would be aided by the near presence of a double ring.

In one of these processes of aggregation a pair is the basic element; in the other, a triplet. The former yields a neutral structure which appears to have no permanent independent existence, unless we suppose it to have escaped detection. What advantage has the one type, or what special disability the other, to account for a difference in probability of existence? The slower velocity of translation in the heavier triplet forms gives greater opportunity for the formation of triplet configurations. The disability may be connected with a tendency of the double ring to attract slowly moving positive electrons within its inner (negative) ring. A formation with a negative ring between two positives *in a plane* is certainly less stable than the structure which has both positive rings in the outer position (as in the triplane), for in the latter less kinetic energy is needed to correspond to a given angular momentum. In virtue of this tendency the double ring may function as a stepping stone to the triplane model.

The disparity in mass between positive and negative

* The other form of triplet, with two positives at the base of an isosceles triangle and a negative at the vertex, may arise from two pairs by supposing a quicker response to repulsion on the part of the negatives, whereby one negative is left to prevent the separation of positives.

electrons makes the latter take the inner place (where the field of force is small), either in the double ring or in the triplane, where nearly equal accelerations are attributed to the two. Kinetic theory connects disparity in velocity of translation with that in mass, and an imperfect attempt to trace this influence has been made in this paragraph. There may be a measure of crudity in thinking of a process of aggregation in this way, but it seems easier to conceive than an addition to a circuit already closed.

XLVIII. *The Partial Tones of the Struck String.*—Part I. *Experimental Investigation of the Fundamental.* *By* Wm. H. George, *M.Sc., University College, Nottingham* *.

[Plates XIII.–XVI.]

Summary.

By harmonic analysis of photographically obtained vibration-curves of the struck string it is found that: (i.) the amplitude of the fundamental is greatest when the string is struck near one of the bridges; (ii.) the position of this maximum point is nearer the bridge the greater the relative mass of the hammer; (iii.) there are other maxima and minima, which become fewer and less pronounced as the relative mass of the hammer is reduced until for the mass-ratio $m/M = 1/2{\cdot}53$, there is only one minimum and two maxima for the whole length of the string; (iv.) the maxima are greater and the minima are less the nearer they are to a bridge.

IT is well known that in a pianoforte the strings are struck near one of the bridges, but the reason for this is not established. The position of the impact has a strong influence on the duration of the impact and upon the pressure law of the impact, and it therefore plays an important part in determining the intensities of the partials in the resulting free vibrations of the string.

In the earliest treatment of the struck string, Helmholtz ('Sensations of Tone,' p. 79 and Appendix v.) was able, by the aid of various assumptions, to determine the amplitudes of the partial tones. Numerical values for five different cases are given, but there is no account of quantitative experimental work undertaken to compare theoretical and experimental values. Helmholtz found, theoretically, that if a string be struck at $1/n$ of its length from one of the bridges then the nth partial would be absent from the resulting free vibrations. He therefore concluded that an

* Communicated by Prof. E. H. Barton, F.R.S.

essential advantage in striking the pianoforte string at 1/7 to 1/9 was that the inharmonic 7th and 9th partials disappear, or at least become very weak.

As early as 1884, A. J. Hipkins (Proc. Roy. Soc. vol. xxxvii. p. 363), and, again, later (*ibid.* vol. xxxviii. p. 83), showed that if a string is struck at 1/8 the eighth partial is not absent. At this time, however, photographic methods of recording the vibrations of any point of the string were not available, and the human ear, often aided by resonators, was largely relied upon to judge the relative intensity of any partial.

The earliest quantitative experimental work was done by Kaufmann (*Wied. Ann.* 1895, vol. liv. pp. 675–712), whose very important paper deals chiefly with the pressure-time law of the impact. He also gives a graphical method for finding the vibration-curve of any point of the string for cases where the pressure law of the impact is known. The graphical method is used because the well-known analytical method would lead to very complicated equations. Included in the experimental work is a set of twenty-six vibration-curves, half of which record the motion of the mid-point of the string, and the other half record the motion of a point of the string distant one-third of its length from the bridge. The string was struck at each of thirteen equidistant points along its length. As a result of these and other experiments, Kaufmann concluded that when the string was struck at about 1/7 to 1/9 of its length the tone was strongest and fullest.

Theoretical work, similar to that of Helmholtz, was later carried out by Delemer (Sci. Abs. A, vol. ix. p. 623, 1906) and by Lamb ('Dynamical Theory of Sound,' p. 74, 1910), who each used different expressions for the pressure-law of the impact. Here, again, no experimental results were given.

In the present work an attempt has been made to systematically investigate the influence of the striking place upon the amplitudes of the partials. As will be seen from the curves, it was also found necessary to study the influence of the relative mass of the hammer. The photographic curves have so far been analysed for the *fundamental* tone only. Whilst the work was in progress a paper by S. K. Datta, on the Das Theory of the Struck String (Proc. Ind. Ass. vol. viii. part ii. 1923) was published. This deals with the mass ratio of hammer and string $m/M = 1{\cdot}687$, and values of the amplitudes of the partials are given for the striking place at 1/9 and 1/10. Also the change in the amplitude

of the fundamental as the position of the impact moves from a bridge along the string up to 1/4 of the length. The experimental method used consisted in measuring with a microscope the amplitude after the string had been struck at the particular place, and then damped at a suitable node for the desired partial. Account has to be taken of the fact that the damping eliminates only those partials which have not a node at the damped point, so that each microscope-reading represents a sum of a number of partials given by A_n, A_{3n}, A_{5n} . . ., etc.

Experimental Method.

In addition to the factors to be studied in the present work, it is clear that the absolute magnitude of the partials will depend upon

(i.) the tension of the string,
(ii.) the length (l) of the string,
(iii.) the velocity (v_0) with which the hammer strikes the string,
(iv.) the optical magnification,
(v.) the time which elapses between the impact and observation of the vibration.

This latter factor must be taken into account since in all practical cases damping is present to an unknown extent. The different partials may die away at different rates, so that it is not necessarily sufficiently accurate to take each record or observation at the same time after the impact.

The photographic records of vibrations reproduced in Plates XIII.–XVI. are all displacement-time curves obtained by shooting the plate upon which the shadow of one point of the string is optically projected.

The apparatus used has already been described in a previous paper (Phil. Mag., July 1924), and, since it includes a timing device, it was possible to obtain in each case a record of the *initial* free vibrations of the mid-point of the string. Some of the curves reproduced on a reduced scale in Plates XIII.–XVI. show even the initial motions, whilst the hammer is still in contact with the string. Errors due to variations of the fifth factor mentioned above are therefore eliminated. By using for any given series of observations the same length of string tuned to the same pitch, the first two factors are kept constant. The third factor, the velocity (v_0), with which the hammer strikes the string, is kept constant by allowing the hammer

to fall always from rest at the same initial inclination (β) with the vertical. From time to time throughout a series of observations, when the initial conditions are shown upon the photographic plate v_0 can be determined from the expression $v_0=(\mathrm{V}\tan\alpha)/(\text{magnification})$, and the result compared with the theoretical value given by $v_0=\sqrt{2gr(1-\cos\beta)}$, where (V) is the velocity of the plate in the vibration camera, (α) is the inclination with the time axis of the initial motion of the observed point of the string, and (r) is the distance between string and axis of rotation of the pendulum. Reference will later be made to the fourth factor, the optical magnification.

The two factors studied throughout this work were the mass of the hammer (m) and the position of the impact (a). By the term "mass of hammer" is here meant the mass of a particle equimomental with the compound pendulum which formed the hammer, so far as rotation about the axis of the pendulum at a distance (r) from it was concerned. The quantity was calculated from the weights and measurements of the complete hammer. The position of the impact (a) was measured by first smoking the string and allowing the hammer to strike once only. The bright speck caused by the removal of the black deposit at the place of impact left a clearly defined mark, from which the distance of the bridge was measured. When the larger string was used (316 cm.) this precaution was not necessary in order to get (a) with sufficient accuracy.

Analysis of Curves.

By recording the vibrations of the mid-point of the string the even-numbered partials were already eliminated from the curves.

Mader Harmonic Analyser.—The results given in Tables I. and II. were obtained by means of the Mader Harmonic Analyser. Before this was possible, the curves had to be enlarged. Now the time axis, which determines the wave-length of the curve, depends upon the speed with which the plate is shot in the vibration camera, and is independent of the optical magnification. On the other hand, the amplitudes of the partials depend on the optical magnification, but are independent of the speed of the plate in the camera. It is clear, then, that all the curves must be magnified by the same amount, and not so as to have the same fundamental wave-length. The Mader Harmonic Analyser was specially convenient for this work, since its readings are

independent of the wave-length of the fundamental provided the curve is properly fixed relative to the instrument and the tracer correctly set upon the tracing-arm before tracing each curve. Each of the original curves reproduced in Plate I. was projected on to a screen and traced by hand, the final wave-length of the fundamental being about 32 cm. in each case. The curves reproduced in Plate XIV. were similarly treated, but, since the pitch of the string was higher, the final wave-length in the curves used on the analyser was about 14 cm. The readings of the sine (S_1) and cosine (C_1) components of the fundamental given in Tables I. and II. are each the mean of three readings, the

TABLE I.—Amplitude of Fundamental (A_1).

Wedge-shaped Metal Hammer $m/M=1$; Length of String $(l)=316$ cm.

Number of Fig. (Pl. XIII.).	a in cms.= Point Struck.	S_1=Mean Sine Component.	C_1=Mean Cosine Component.	$A_1 = \sqrt{S_1^2+C_1^2}$.
1	11·0	+2·065	+1·005	2·297
2	14·37	+2·89	+0·635	2·959
3	16·1	+3·16	+0·505	3·00
4	20·3	+3·792	+0·07	3·793
5	28·3	−4·685	+0·41	4·703
6	34·4	−4·793	+0·05	4·793
7	41·6	−5·235	−0·078	5·236
8	48·2	+5·33	+0·435	5·348
9	53·6	+4·97	+0·093	4·972
10	62·4	+4·093	+0·02	4·090
11	69·7	−2·91	+0·135	2·913
12	75·5	+2·395	+0·246	2·407
13	81·75	−1·935	−0·61	2·029
14	86·75	−1·413	−0·08	1·415
15	92·0	−1·01	+0·10	1·015
16	97·0	+1·066	−0·10	1·071
17	100·0	+1·17	+0·03	1·171
18	105·3	−1·79	−0·12	1·794
19	110·3	+2·445	+0·20	2·453
20	116·1	+2·52	−0·57	2·584
21	120·2	−2·42	+0·82	2·555
22	128·2	−2·73	+0·21	2·738
23	144·3	+2·613	−0·10	2·615
24	139·55	+3·02	−0·07	3·021
25	134·8	−2·865	+0·09	2·866

last column showing the amplitude (A_1) of the fundamental obtained by taking the square root of the sum of the squares of the sine and cosine components. The readings are in centimetres.

TABLE II.—Amplitude of Fundamental (A_1).

Wedge-shaped Metal Hammer $m/M = 9{\cdot}625$; Length of String (l) = 100 cm.

Number of Fig. (Pl. XIV.).	a in cms. = Point Struck.	S_1 = Mean Sine Component.	C_1 = Mean Cosine Component.	$A_1 = \sqrt{S_1^2 + C_1^2}$.
1	1·43	−2·52	−0·34	2·54
2	3·52	−4·475	−0·035	4·475
3	5·58	−3·47	−0·13	3·47
4	6·37	+2·61	−0·01	2·61
5	7·27	−1·595	+0·02	1·59
6	8·20	−0·56	−0·125	0·57
10	10·6	+1·91	−0·07	1·91
11	11·7	−2·725	−0·16	2·73
12	14·0	−3·99	−0·15	3·99
13	15·18	−3·87	−0·15	3·87
14	16·3	−3·23	−0·08	3·23
15	17·75	−2·345	−0·26	2·36
16	19·94	−1·16	−0·05	1·16
17	22·6	−1·10	−0·805	1·36
18	25·05	−2·405	−0·005	2·405
19	27·8	−3·59	−0·40	3·61
20	30·6	−2·47	−0·19	2·48
21	33·58	−2·115	−0·09	2·12
22	36·9	−1·945	−0·03	1·95
23	41·9	−2·635	−0·265	2·65
24	50·0	+3·395	−0·65	3·45

Graphical Method.—The curves of Plates XV. and XVI. had previously been analysed by a graphical method, which consisted in removing the partials one at a time until the resulting curve looked like a pure sine curve. The amplitude of this remaining curve then gave the amplitude of the fundamental. To remove any given partial, a tracing of the vibration-curve was moved along the axis of the original curve a distance of *half* the wave-length of the partial which it is desired to remove. The ordinates were then added algebraically at a sufficient number of points, and the new curve drawn through these points represented the original curve with one partial removed.

RESULTS.

The results of four sets of analyses are best seen in detail in figs. 1–4, in which the amplitudes of the fundamental are plotted against the distance (a) of the striking place from the nearer bridge. For the heaviest hammer (see fig. 2)

Fig. 1.

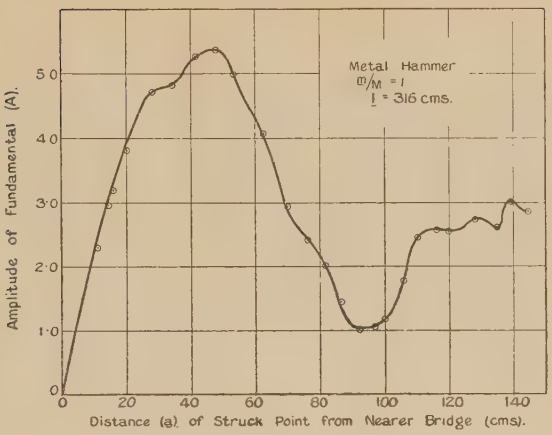


Fig. 2.

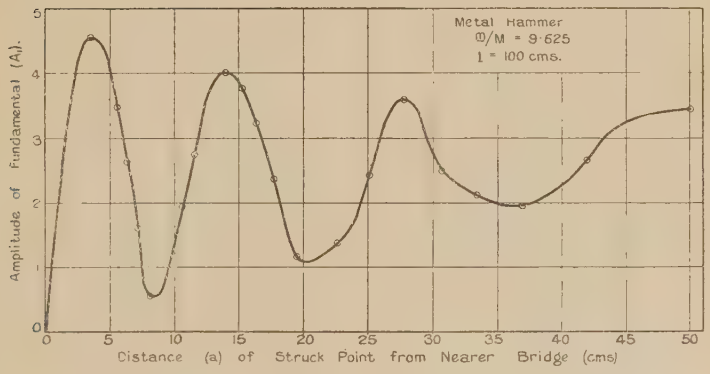


Fig. 3.

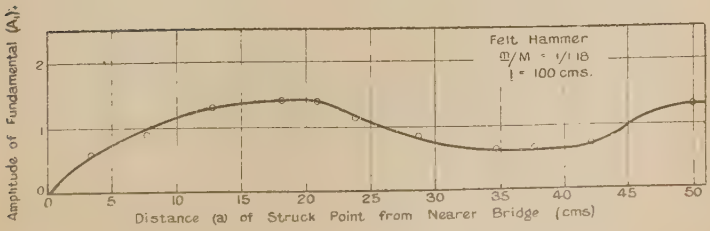

Felt Hammer
m/M = 1/118
l = 100 cms.
Amplitude of Fundamental (A).
2
1
0
0 5 10 15 20 25 30 35 40 45 50
Distance (a) of Struck Point from Nearer Bridge (cms)

Fig. 4.

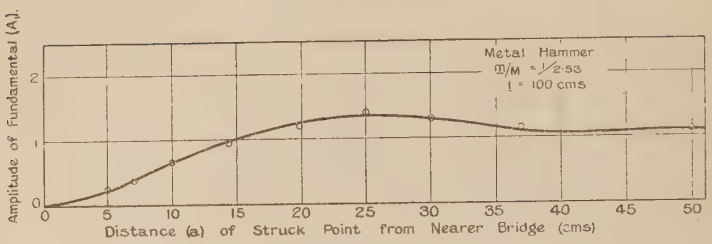
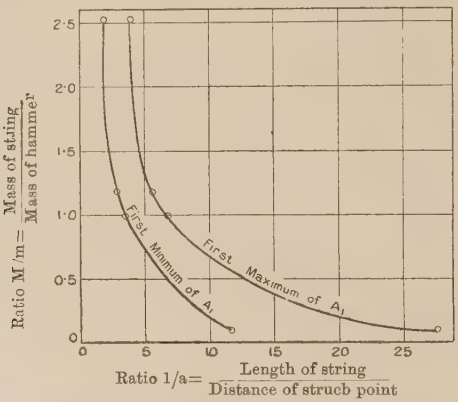


Fig. 5.

Influence of M/m upon positions of Struck Point for the first maximum and the first minimum values of the amplitude (A_1) of the fundamental.


Ratio M/m = Mass of string / Mass of hammer
First Minimum of A1
First Maximum of A1
Ratio 1/a = Length of string / Distance of struck point

there are for the whole string seven places at which the amplitude rises to well-marked maxima and six corresponding minima, whilst for the lightest hammer (see fig. 4) there are only two maxima and one minimum. The results may be summarized thus :—

(i.) The amplitude of the fundamental is greatest when the string is struck near one of the bridges.

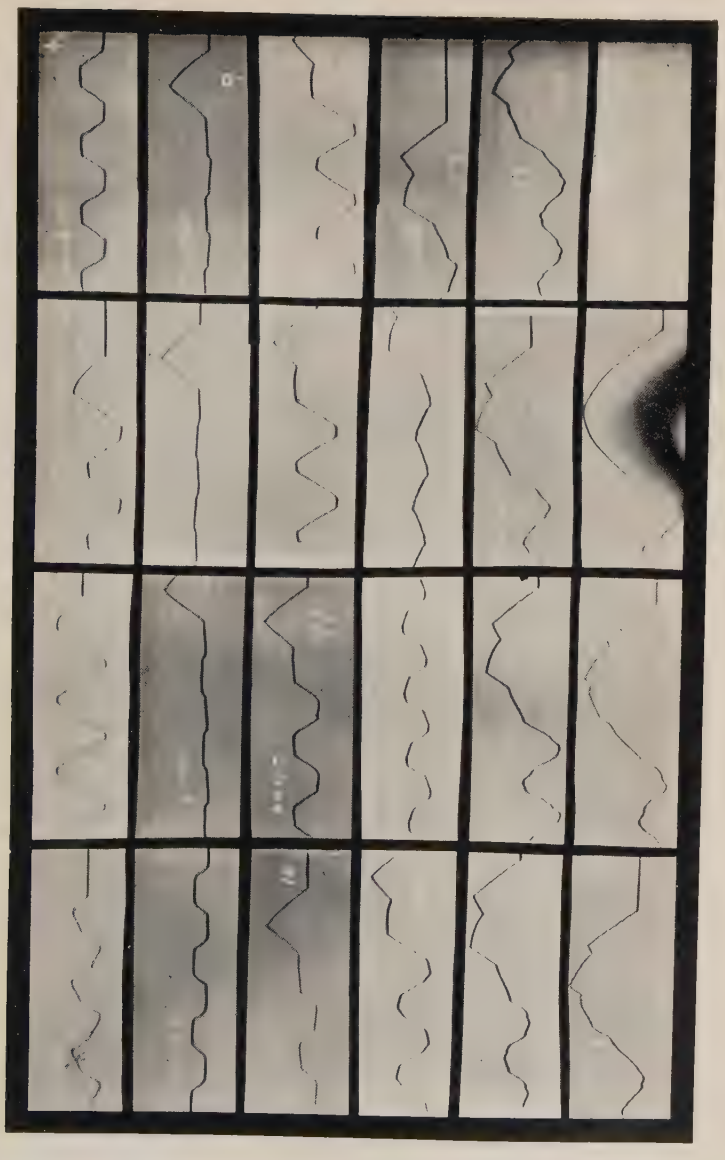
(ii.) The position of this maximum point is nearer the bridge the greater the relative mass of the hammer (fig. 5).

(iii.) There are other maxima and minima points which become fewer and less pronounced as the relative mass of the hammer is reduced, until for the mass-ratio (m/M = 1/2·53) there is only one minimum and two maxima for the whole length of the string.

(iv.) The maxima are greater and the minima are less the nearer they are to a bridge.

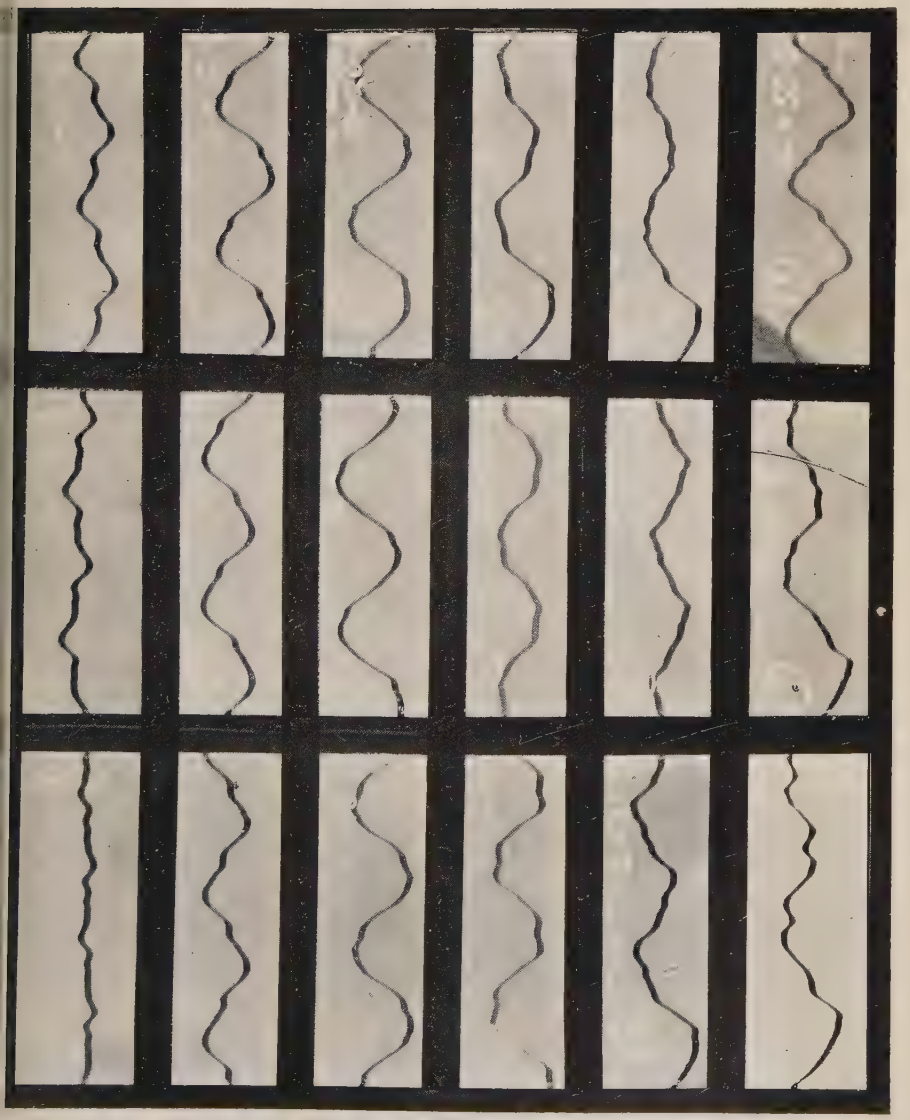
Vibration Curves of the Mid-Point of the String.

Metal Hammer $m/M=1$; $l=316$ cm. ; $a=$Distance of Struck Point from Nearer Bridge ; Linear Density (μ) of Wire $=0{\cdot}093$ gm. per cm. ; Time Axis is Positive from left to right. Fig. 19 shows Initial Conditions.



Vibration Curves of the Mid-Point of the String.

Metal Hammer $m/M = 9{\cdot}625$; $l = 100$ cm.; a = Distance of Struck Point from Nearer Bridge; Linear Density (μ) of Wire = 0·0174 gm. per cm.; Time Axis is Positive from right to left. All figures except Nos. 4, 5, and 15 show Initial Conditions.



Vibration Curves of the Mid-Point of the String.

Felt Hammer $m/M = 1/1{\cdot}18$; $l = 100$ cm.; a = Distance of Struck Point from Nearer Bridge; Linear Density (μ) of Wire = 0·093 gm. per cm.; Time Axis is Positive from left to right. Initial Conditions can be seen in Figs. 5, 6, 8–13, 15–18.

Vibration Curves of the Mid-Point of the String.

Metal Hammer $m/M = 1/2{\cdot}53$; $l = 100$ cm.; a = Distance of Struck Point from Nearer Bridge ; Linear Density (μ) of Wire = 0·093 gm. per cm.; Time Axis is Positive from left to right. Fig. 17 shows Initial Conditions.

Attention is drawn to the figs. 7, 8, and 9 of Plate XIV., which show that the fundamental is hardly excited at all in these particular cases, and a change of 0·12 cm. in the position of the impact is sufficient to make an appreciable difference in the amplitude of the vibration (figs. 7 and 8). All the figures on this Plate, except figs. 4, 5, and 15, show the initial motions of the observed point. As the position of the impact gets nearer the observed point, the successive reflexions at the hammer during the impact can be seen. It is hoped that by the oscillograph method (see Roy. Soc. Proc. A, vol. cviii. pp. 284–295 (1925)) and the use of a carbon contact it will be possible to detect all the corresponding pressure-changes at the hammer under conditions like these.

In Part II. of this paper it is hoped to give the theoretical amplitudes of the partials derived by the well-known method (Rayleigh, 'Sound,' vol. i. § 130) and to compare these results with the experimental ones here given, the harmonic analysis of the curves being completed for the other partials.

University College,
Nottingham,
April 1925.

XLIX. *Notices respecting New Books.*

The Theory of Relativity. By L. Silberstein, Ph.D. Second Edition, enlarged. [Pp. x+563 with 24 figures.] (London: Macmillan & Co., 1924. Price 25*s.* net.)

THE first edition of this work, published in 1914 and dealing with the restricted theory of relativity, is well known. This is reprinted with very few changes as Chapters I. to X. of the present book. In spite of the development of the tensor calculus, which forms a weapon of very great power for attacking the problems of generalized relativity, the author has adhered to the ordinary vector analysis and quaternions in dealing with the restricted theory. There is much to be said for this course; the older methods are amply sufficient for their purpose, and their physical interpretation is more easily comprehended by the beginner. Of the new matter in this edition, Chapters XI. to XIV. deal with the generalized theory and the crucial phenomena; Chapter XV. deals with the attempts of Weyl and others to bring electromagnetic phenomena into the generalized relativity scheme;

and Chapter XVI. is devoted to cosmological speculations. A series of miscellaneous notes are added at the end, explanatory of, or supplementary to, various matters discussed in these chapters.

The treatment is admirably clear throughout. The author has been at considerable pains to distinguish between the metrical and non-metrical properties of tensors, and to make clear the physical meaning of the analysis and the results. Students of very modest mathematical attainments will therefore be able to read the volume with profit. The author avoids the paradoxical methods of presentation which have marred some treatments of the theory and which have increased the difficulties of the student. The treatment of the subject is in many respects novel, and it is evident that great care has been taken to minimize the difficulties—conceptual and analytical—of the theory.

The last chapter is the one in which there is the greatest divergence from other treatises on the theory. A detailed study is given of both Einstein's and de Sitter's cosmologies. The author explains clearly why, in his opinion, Einstein's cosmology is untenable. The generalized Doppler effect, due both to distance and to line-of sight motion, is explained in detail, and the radial velocities of special nebulæ are used to derive an estimate of the curvature radius of de Sitter's space-time. This portion of the subject is still very speculative, but the author's discussion appears to give substantial support to de Sitter's cosmology. We are grateful to the author for this detailed account of a part of the theory which has been much neglected.

Full references to original papers are given throughout.

In conclusion, we may say that we do not know a better or more complete exposition of the theory of relativity than that under review.

Introduction to Theoretical Physics. Volume I. By Arthur Haas, Ph.D., Professor of Physics in the University of Vienna. Translated by T. Verschoyle, M.C., B.Sc., A.R.C.S. [Pp. xiv + 331 with 58 figures.] (London: Constable & Co., 1924. Price 21*s.* net.)

The days when the various branches of physics could be treated as isolated units are long past. Modern physics is, however, such a vast subject that a text-book of reasonable size can deal with only one branch or portion of one branch. There is, therefore, a real need for a book in which the various branches of the subject are developed in connexion with one another and with a consistent notation. Such a volume can necessarily not be exhaustive, but should deal with fundamental principles in a stimulating manner so that the student or worker in other branches of science will have a well-balanced view of the whole subject and of the relationship of its different parts. Christiansen's

'Elements of Theoretical Physics' was a book of this nature, but was published 30 years ago and is now in many respects out of date. All students of science should, therefore, be very grateful to Professor Haas not merely for filling this gap in scientific literature, but for filling it in such an excellent manner. A judicious selection of material, combined with a mathematical treatment in which successive steps are carefully explained, render the volume one which can be read with profit by the student of every branch of science, even though his mathematical equipment is of the slenderest.

At present only Volume I. is available in the English translation. It is to be hoped that Volume II. will shortly be published. The first volume is divided into two parts dealing respectively with mechanics, including the general theory of vector fields, of vibrations and of potential, and the theory of the electromagnetic field and of light. We are glad to see vector notation and analysis used from the beginning; frequently the student makes his first acquaintance with the vector notation when he begins to study the electromagnetic theory, whereas many problems in mechanics such as the rotation of a rigid body about a fixed axis lend themselves admirably to vector methods. Professor Haas has the happy gift of being able to condense a large amount of material in concise yet readable form, and it is surprising what a wide field is covered in about 300 pages. A summary of the contents is given at the end which is valuable not only for reference purposes, but also to enable the student more easily to trace the connexion between different portions of the argument.

The volume is one which can be thoroughly recommended to and should be read by every serious student of science.

The Principle of Relativity. A Collection of Original Memoirs on the Special and General Theory of Relativity. By H. A. Lorentz, A. Einstein, H. Minkowski, and H. Weyl. With Notes by A. Sommerfeld. Translated by W. Perrett and G. B. Jeffery. (Methuen: London. 12*s.* 6*d.*)

It is a great convenience to have between one pair of covers the important original papers contained in this volume. There is first, part of the classical paper by Lorentz on Michelson's Interference Experiment, written in 1895, followed by his paper on Electromagnetic Phenomena in a system moving with any velocity less than that of Light, which appeared in 1904. Then come Einstein's papers on the Electrodynamics of Moving Bodies, which originally appeared in the *Annalen der Physik* in 1905, and his short paper on the Dependence of the Inertia of a Body on its Energy Content, published in the same issue of that journal. Next comes the paper by Minkowski on Space and Time, which will be for ever a classic, which he gave as an address

to a congress of physicists in Cologne in 1906. There is a valuable appendix to this paper in the form of notes by Sommerfeld. Weyl is represented in this volume by a reprint of his paper on Gravitation and Electricity, from the *Sitzungsberichte der Preussischen Akad. d. Wissenschaften*, 1918.

The other half of the volume is wholly a reprint of Einstein's later papers. There is the paper on the Influence of Gravitation on the Propagation of Light, from the *Annalen der Physik*, 1911. Next, the Foundation of the General Theory of Relativity, from the same journal in 1916. Next there is the paper on Hamilton's Principle and the General Theory of Relativity, from the *Sitzungsberichte der Preussischen Akad. d. Wissenschaften*, 1906. Finally there are the papers originally published in this same journal in 1917 and 1919 respectively on Cosmological Consideration on the General Theory of Relativity, and the paper entitled "Do Gravitational Fields play an Essential Part in the Structure of the Elementary Particles of Matter?"

It will be seen that the contents of this book make it of the very greatest value as a convenient reference book for the progress of the theory of relativity in the work of Einstein through its first two stages. The addition of the other very important papers further increases its value. The translators are to be congratulated very heartily on their achievement.

Einstein's Theory of Relativity. By Max Born. Translated by H. L. Brose, M.A. (Methuen: London. 12*s.*)

This book is a translation of the third edition of Born's book which appeared originally in German in 1900. The idea of the book, according to the author, was to give an exposition of the Theory of Relativity *ab initio*, which could be followed by those who have very little knowledge of mathematics or physics. Professor Born set out on this rather formidable task by discussing at some length, with the help of a number of experiments, the classical conceptions of velocity, acceleration, mass, force, and so on. The reader is then brought by easy stages all the way to the general Theory of Relativity. Professor Born has evidently expended a great deal of care on developing all the points in the easiest and simplest fashion for the audience which he has in view, and those students who have an ambition to understand the Theory of Relativity in spite of a meagre equipment in mathematics and physics would find it worth while to study this book. The translation appears to be very satisfactory.

Space and Time. By Carl Benedicks. With an Introduction by Sir Oliver Lodge. (Methuen. 4*s.*)

This small thin volume is an essay embodying Professor Benedicks's views on the foundations of new theories. His

purpose is not to understand them in themselves, but to discuss how far they are necessary or not from the standpoint of science in general. The essay is based on an address given to the Students' Club in Stockholm, and though quite slight, it is interesting and well worth reading.

The History of Mathematics in Europe. By J. W. N. Sullivan. (Pp. 109, with 17 illustrations.)
Electricity and the Structure of Matter. By L. Southerns, M.A., B.Sc. (Pp. 128, with 34 illustrations.)
("The World's Manuals": Oxford University Press, 1925. Price 2*s.* 6*d.* net each).

These two volumes are included in a new series, entitled 'The World's Manuals,' which are in course of publication by the Oxford University Press. The series is designed to provide the student who is undertaking a special study with the broad outlines and guiding principles of his subject, and also to be of interest to the great body of general readers who welcome accurate and concise accounts of subjects of general interest. The two volumes under review are included in the section "Science and the History of Science." The first of the two is one of the subseries, "Chapters in the History of Science," the general editor of which is Dr. Charles Singer. It traces in outline the development of mathematics from its beginnings in Europe up to the time of the rise of the conception of mathematical rigour. The contributions by the principal mathematicians of the period covered are carefully summarized. Specimens of actual solutions of several problems (in modern notation) and also of notation from early mathematicians are given. These enable the reader more clearly to realize to how great an extent successive advances were dependent upon the improvement of the notation in use and the better to understand the quality of their achievements. The second volume gives a brief outline of the history of the subject dealt with up to the time of the discovery of the electron, followed by an account of some of the older and also of the principal modern applications and developments of electricity, both theoretical and practical. These include radio-activity, the structure of the atom, electromagnetic waves, and the use of X-rays for the study of crystal structure.

Both volumes are written in a scholarly manner and form concise and accurate summaries of the subjects dealt with. They can be thoroughly recommended both to the scientific and also to the general reader.

L. *Intelligence and Miscellaneous Articles.*

THE CONSTANT N OF AVOGADRO.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I HAVE just read in the April issue of the Phil. Mag. the letter of Mr. L. M. Alexander, Assistant Professor of Physics in Cincinnati, concerning my paper "A New Determination of the Constant N of Avogadro," which was published in the Philosophical Magazine, 1924, xlviii. p. 664, and I wish to thank him for the opportunity that he gives me of correcting myself.

Of course, his criticisms of the two estimates of the per cent. error involved in the calculations are obviously true. But I did not say in my paper that my value and that of Millikan agreed within the experimental error, although the difference of 1 per cent. is small. Thus, one should read 1 per cent. instead of 0·1 per cent., and $\pm 0{\cdot}009$ instead of $\pm 0{\cdot}08$.

As to the third objection, which is also very obvious, it was not even necessary to use so many formulas to reach the conclusion that, having started from a value of the area obtained from the knowledge of A, surface of adsorption, one was bound, after cancellation, to reach the conclusion that $A = A$, unless the arithmetic had been wrong. Unfortunately, this identity did not strike me before the paper was out, and I plead guilty to the oversight. I may add that I corrected these three errors in a subsequent paper on the same subject, which I sent to the 'Journal de Physique,' and which was received in Paris on the sixth of January, 1925, long before I read Professor Alexander's letter. This paper is now in the press, and would have been out before if it had not been delayed by a printers' strike.

However, I wish to emphasize the fact that none of these errors invalidated in any way the experimental work, or the conclusions drawn from it.

I take this opportunity to correct another slight mistake which Professor Alexander has overlooked. The real value of N obtained from my experiments should read

$$N = 6{\cdot}004$$

instead of 6·003.

With many thanks for your courtesy, I remain

Yours very truly,

LECOMTE DU NOÜY.

The Rockefeller Institute,
New York,
May 28, 1925.

(P. Lecomte du Noüy, Sc.D.)

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]